DEVELOPMENT OF A RATIONAL CHARACTERIZATION METHOD FOR IOWA FLY ASH

ANNUAL PROGRESS REPORT 1
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IOWA DOT PROJECT HR-286
ERI PROJECT 1847

Sponsored by the Highway Division of the
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ENGINEERING RESEARCH INSTITUTE
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INTRODUCTION

The following report summarizes research activities on the project for the period December 1, 1985 through November 31, 1986. Research efforts for the first year have proceeded basically as outlined in the project proposal.

RESEARCH APPROACH

The preliminary work presented in the proposal had indicated that there were fundamental differences in physical properties of hydrated fly ash that were not evident from ASTM C 618 chemical and physical test results.

As a first step in the project, data from ASTM C 618 testing was compiled for ashes from selected power plants. These data were analyzed statistically. Additional physical testing of fly ash pastes was conducted to confirm the preliminary findings.

Ashes from the Council Bluffs, Lansing, Ottumwa, and Neal 4 power plants were selected to represent the range of ASTM Class C ashes available in Iowa. Operating details of these plants are given on Table 1. All plants burn low-sulfur coal from the Powder River basin near Gillette, Wyoming.

Samples of these ashes, for testing and use on the project, were supplied through the cooperation of Mr. Lonnie Zimmerman of Midwest Fly Ash and Materials, Inc., Sioux City, Iowa. The sampling procedure used is prescribed in

TABLE 1

Power Plant Details

Power Plant	Boiler Type	Generating Capacity (NET MW)	Annual Ash Production (Tons/yr)	Precipitator Type	Year on Line	Ash Silo Storage Capacity (Tons)	Coal Source
Council Bluffs #3	Babcock-Wilcox	700	90,000	H-ESP (Na_2CO_3 added to aid precipitator)	1978	2,500	Wyoming (Eagle Butte & Bell Ayr mines)
Lansing #4	Rilley-Stoker	260	28,000	H-ESP	1977	200	Wyoming (Eagle Butte & Bell Ayr mines)
Ottumwa	Combustion Engineering	675	80,000	H-ESP (Na_2CO_3 added to aid precipitator)	1981	3,500	Wyoming (Sunedco-Cordero mines)
Port Neal #4	Foster-Wheeler	600	80,000	H-ESP (Na_2CO_3 added to aid precipitator)	1979	5,000	Wyoming (Rawhide mine)

H-ESP = Hot side electrostatic precipitator.

ASTM C 311. Grab samples of each ash truck (approximately 20 tons) exiting the plant were taken. After 20 grab samples were taken they were combined to form a composite sample representing about 400 tons of fly ash.

ASTM PHYSICAL AND CHEMICAL TESTS

As a part of other research, the Materials Analysis and Research Laboratory (MARL) has been establishing an on-going data base of ASTM test results for Iowa fly ashes [1]. Fly ash testing for physical and chemical properties was accomplished by using methods similar to those specified in ASTM C 311. Quantitative x-ray fluorescence spectrometry (QXRF) was used for elemental analysis. These data for 1983, 1984, and 1985, and the statistical analyses, are reproduced in Tables I, II, and III in Appendix A.

Table I (Appendix A) summarizes the data obtained from the fly ash samples subjected to chemical and physical analysis. Table II summarizes the data obtained from the physical testing conducted on each 400 ton lot of fly ash. The data listed in Tables I and II were obtained from fly ash samples collected from the various power plants at unequal intervals from 1983 to 1985. The majority of the samples were obtained between April and October of each year (i.e., the portland cement concrete construction season). In Tables I and II, $\overline{X}$ refers to the arithmetic mean, S refers to the standard deviation,

R refers to the arithmetic range and n refers to the number of samples. In general, the analytical results listed in the two tables have been reported to more significant figures than were actually obtained from the analyses. This was done so that additional statistical quantities (i.e., coefficient of variation, etc.) could be calculated from the tables without experiencing severe rounding errors. Table III lists the data for the Type I portland cements used for evaluating the pozzolanic activity of the fly ash samples. Note that during 1984 and 1985 two different lots of cement were used each year for evaluating pozzolanic activity. The cements were from the same manufacturer but they were obtained at different times, and consequently represent different lots. The compressive strength values listed in Table III are the averages of the control samples for that year.

Figure 1 illustrates typical x-ray diffractograms of fly ashes obtained from the four different power plants. The crystalline compounds present in all of the fly ashes were: alpha quartz, anhydrite, calcium oxide, magnesium oxide and a mineral similar to tricalcium aluminate. The fly ashes may also contain small amounts of a compound similar to tetracalcium trialuminate sulfate. The major type of glass found in all of the fly ashes had an amorphous scattering hump above 30 degrees 2-theta (Cu K-alpha radiation). The fly ashes exhibit similar mineralogies, the differences being

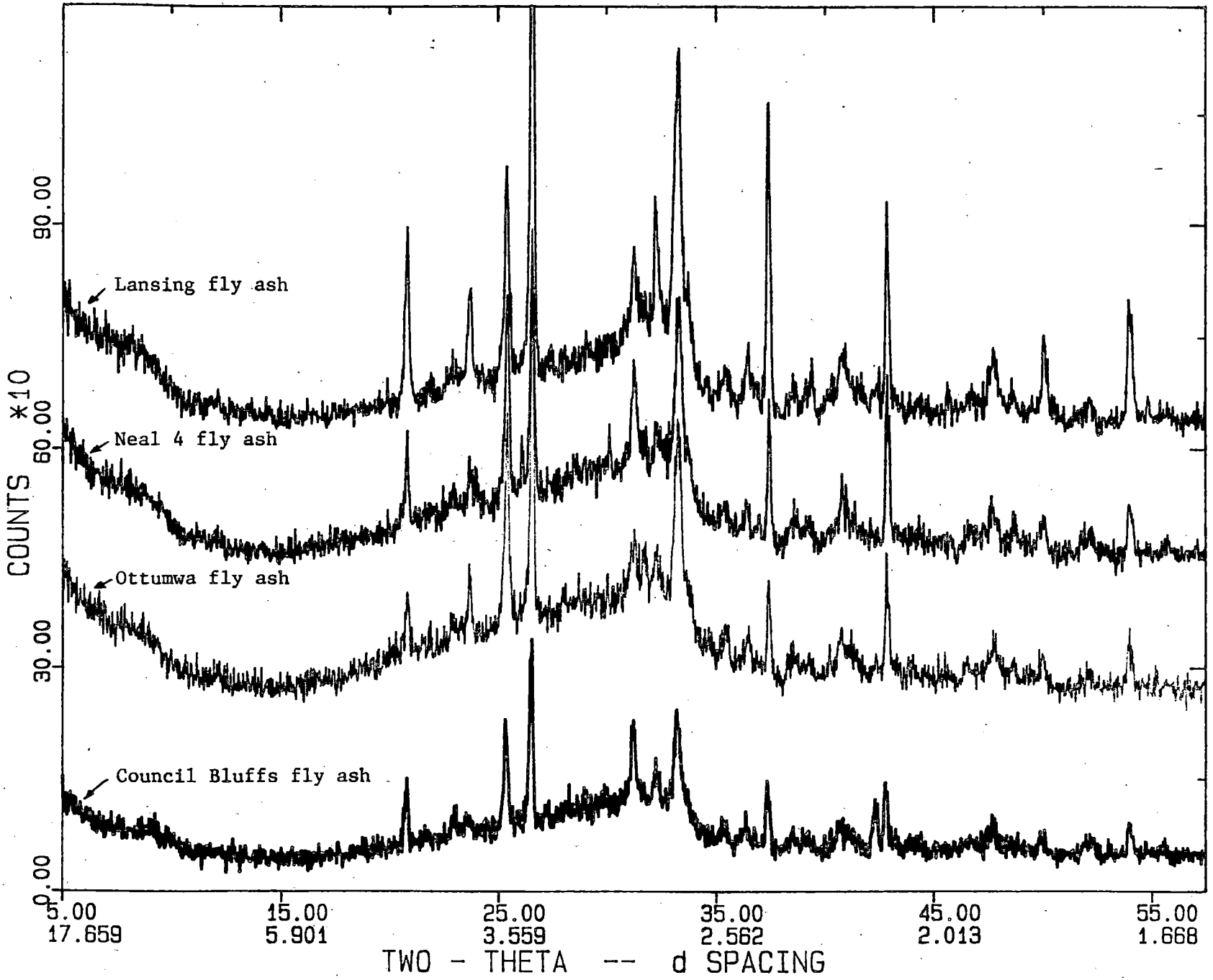

Figure 1. Typical x-ray diffractograms of fly ash from the four power plants.

due mostly to concentration rather than mineral structure.

The evaluation of the foregoing data is briefly summarized as follows.

Chemical Tests

Overall, the variation of the mean chemical composition for each individual power plant as a function of time is not very large. The coefficient of variation for the major elements (Si, Al and Ca - expressed as oxides) was typically about 10 percent during the three years of monitoring. Sulfur, sodium and phosphorus exhibited the largest coefficients of variation of the 10 elements (expressed as oxides) measured. There appears to be a general trend which indicates an increase in the concentration of sulfur in most of the fly ashes, from 1983 to 1985. Also, sulfur exhibits a fairly wide range of concentration at any given power plant during a single year. The average concentration of sodium is fairly constant at each power plant over the three year monitoring period. This can be attributed to the fact that three of the four power plants add sodium carbonate to the raw coal to enhance the efficiency of their electrostatic precipitators. The process, which appears to be cyclical, starts with the addition of small amounts (or none) of sodium carbonate to the raw coal feed when the precipitator plates are clean and highly efficient. As the precipitator plates become less efficient, the amount of sodium carbonate added to the raw

coal feed is increased to enhance the precipitator's efficiency. When the upper limit of sodium carbonate addition is reached (i.e., boiler slagging becomes excessive) the precipitator plates are cleaned and process starts again. It appears that in the majority of the Iowa power plants studied this results in a bulk annual (average) concentration of about 1.9 to 2.1 percent sodium oxide. Presently the significance of the phosphorus content of our high-calcium fly ashes is not clear. It is apparent from Table I (Appendix A), that the concentration of phosphorus varies dramatically in the fly ashes studied. Phosphorus pentoxide is one of the glass network forming oxides and it is speculated that it should contribute to the amorphous (glassy) phase of a given fly ash.

The available alkali test results indicate that the fly ashes contributed about 65 percent of their total alkali oxide concentration to the test pore solution during the 28 days of curing. The results from several of the fly ashes show the same cyclical pattern that was observed for the total sodium concentration. Other research at MARL [2] indicates that for all four of the fly ashes being studied, the alkalis in the fly ash are still contributing significantly to the alkalis measured in the pore solution at curing times of well over 100 days. Hence, the required 28 day curing period is quite arbitrary and really does not

reflect the total amount of alkalis that can be dissolved from the fly ash into the pore solution.

In summary, the variation in the mean chemical composition for each individual power plant was not very large during the monitoring period. Sulfur, sodium and phosphorus, among the 10 elements studied, exhibited the largest coefficients of variation.

Physical Tests

Analysis of the ASTM physical test results [1] yielded the following conclusions.

Moisture content and loss on ignition test exhibited stable mean values, but rather large variability. The variability is not significant from a practical standpoint.

Fineness tests consistently exhibited the largest coefficients of variation for any of the physical test that produced significant results. The mean fineness values, however, were fairly stable over the monitoring period.

None of the fly ash samples tested during the 3 year monitoring period failed the autoclave test.

The specific gravity of fly ash samples obtained from a single power plant have stable means and small coefficients of variation during any single year. Specific gravity of a fly ash, however, may change significantly from year to year.

Pozzolanic activity tests (both 7 and 28 days) indicate that mortars containing the various fly ashes reach about 90 percent of the strength of the portland cement control samples.

Mortars containing 35 percent (by volume) replacement of fly ash for cement showed reduced mixing water requirements when compared to the portland cement control mortars. The reduction in mixing water was typically 5 percent to 10 percent.

The results of this work confirm the proposal hypothesis that little variation in physical and chemical properties is observed for fly ash from a given generating station, as measured by ASTM tests.

EXPERIMENTAL PROGRAM

In order to verify the proposal hypothesis and to provide data for a potential characterization method, additional testing was initiated on fly ash paste samples from the

selected power plants. The physical testing conducted on fly ash paste mixes is shown on Figure 2. All fly ash pastes were prepared at a water/fly ash ratio of 0.27 and the following tests conducted.

1. Compressive strengths were measured on one inch cube samples tested at 4 hours, and 1, 3, 7, 14, and 28 days of moist curing.

2. Shrinkage/expansion characteristics were measured from one by one by eleven inch prisms. Two specimens were cast from each mix. One sample was moist cured, the other was cured under ambient room conditions of temperature and humidity. Length measurements were taken periodically in accordance with ASTM method C 490.

3. Setting properties were evaluated using a soil pocket penetrometer. Test sample container size was about 4 inches in diameter by 1 inch in depth. Penetrometer readings in tons per square foot were taken as a function of time. Initial set was defined as the first discontinuity in the pressure versus time curve. Final set was arbitrarily defined as 4.5 tons per square foot penetrometer bearing pressure.

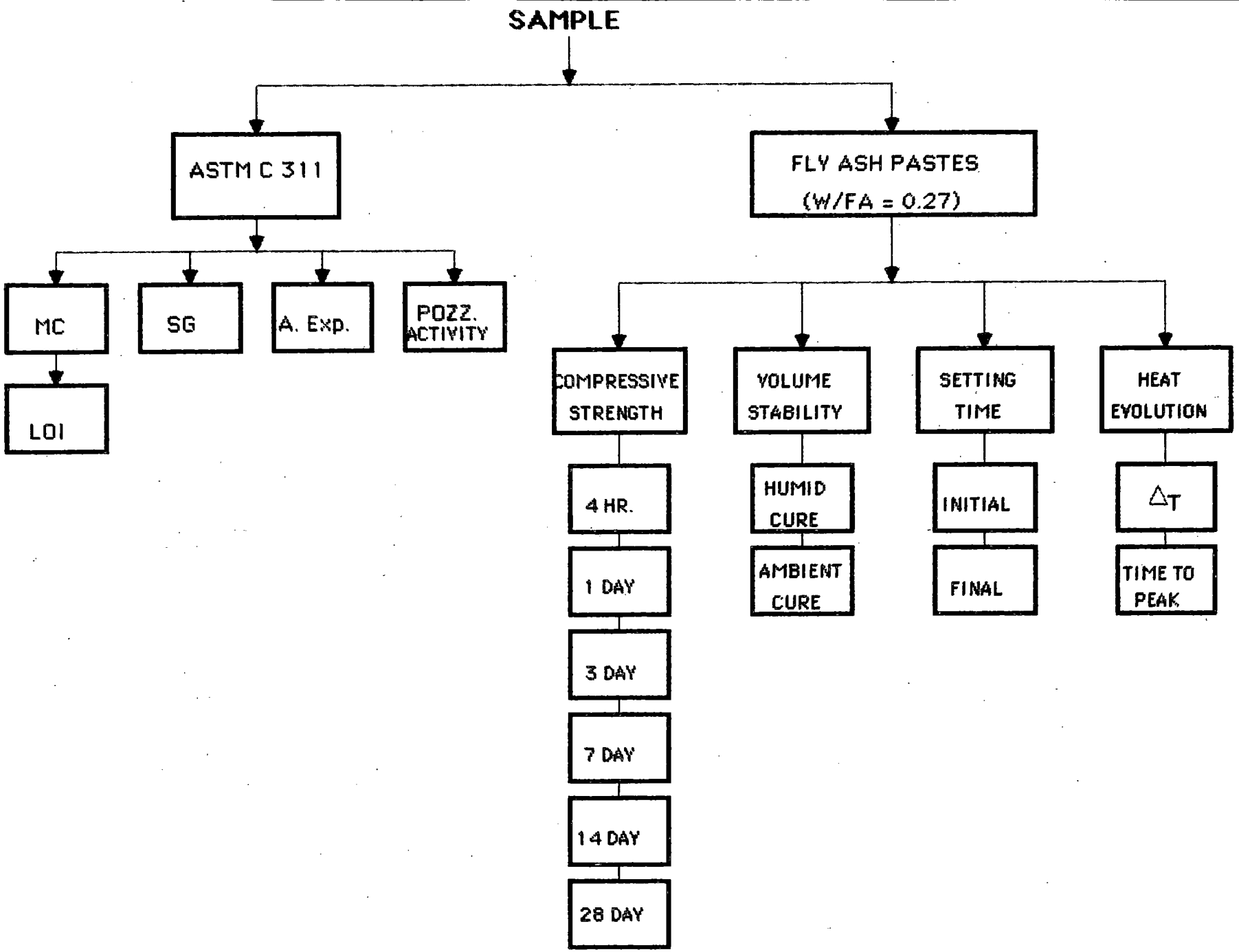

Figure 2. Physical testing program for fly ash pastes.

4. Calorimetric properties of hydrating fly ash/water slurry systems (10 gm fly ash to 28.5 gm water) were evaluated using a sealed DeWar flask and a temperature recording system. The heat evolution was defined as the temperature differential between the start of the test and the maximum temperature measured during the test.

Fly ash from the Ottumwa generating station is heavily used during the construction season; therefore, more samples and test results were generated from that source. The following discussion will be based on the Ottumwa data with reference to trends displayed by the ashes from other plants. Since the Neal 4 plant was shutdown this year, it was dropped from the monitoring schedule.

Physical Tests

The results of 28 day compressive strength development of one inch cube samples for the Ottumwa ash are shown on Figure 3. The trends for the 4 hour, and the 1, 3, 7, and 14 day tests were similar and are given in Appendix B. It is evident from Figure 3 that extreme variations in strength development (by a factor of 6 times) can and do occur. This variation appears to be cyclical around the summer period, with a base level of approximately 1000 psi from samples obtained during spring, fall and winter. Data for ashes from the Lansing and Council Bluffs sources are indicating similar trends as

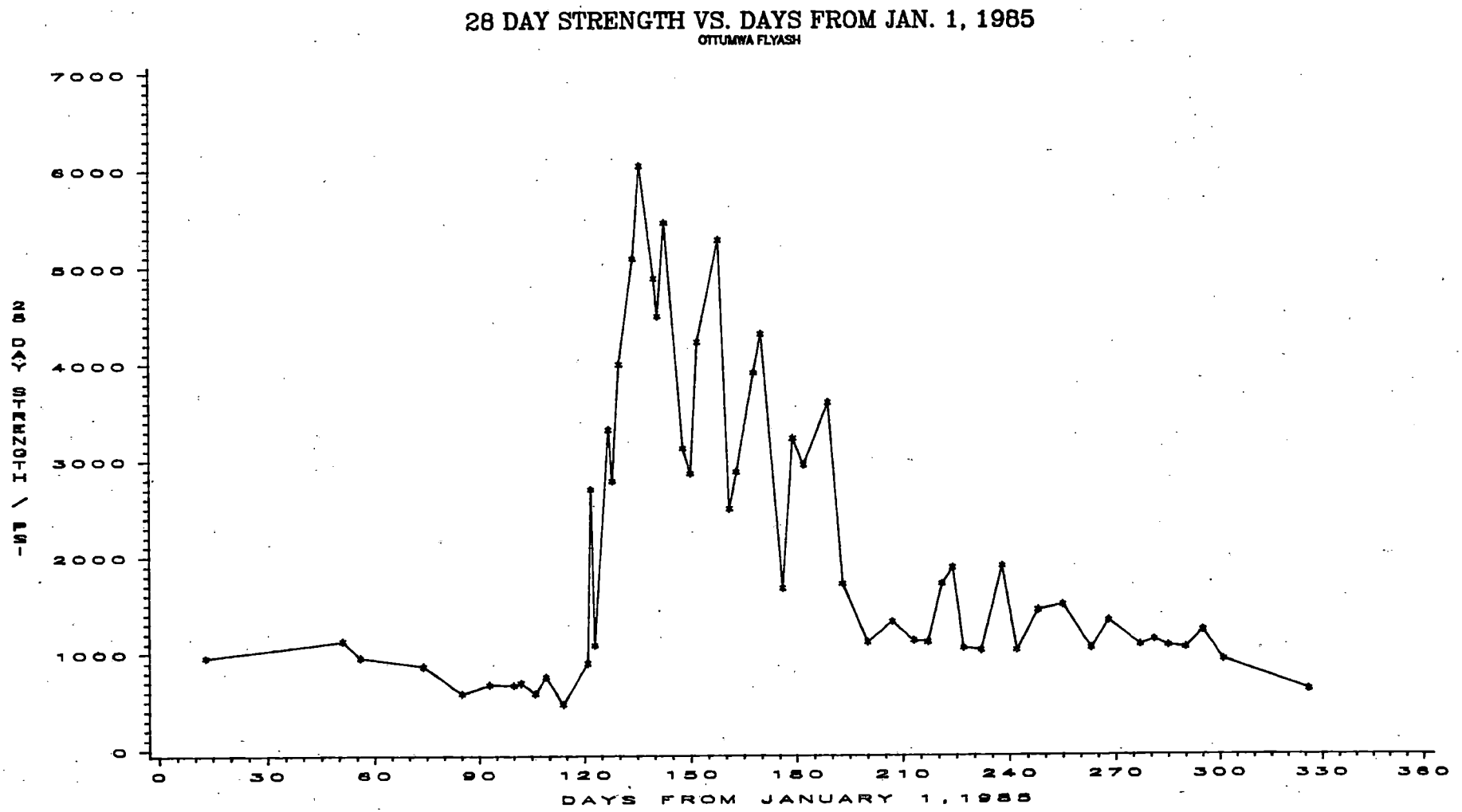

Figure 3. Compressive strength development of paste cubes, Ottumwa fly ash.

shown on Figure 4. Additional test results currently being obtained for 1986 production samples appear to be confirming the cyclical trend and extreme strength development variation. We currently believe this variation may be a function of the plant maintenance schedules and sodium carbonate coal treatment levels and loading rates. This will be investigated in detail during the second year of monitoring.

IDOT routinely runs fly ash mortar cube tests using Iowa test method No. 212. Data on these test results were supplied to the project by Jeff Nash. Figures 5 and 6 present the 1 and 7 day test results using Ottumwa fly ash from 1983 through 1986. Again, extreme variations are evident, and they appear to be cyclical. The mortar cube strength variations are obviously being caused, in the most part, by the percent replacement fly ash in the mortar mixes. IDOT mortar cube test results for the Council Bluffs, Lansing, and Neal 4 plants are given in Appendix C and confirm similar cyclical trends for ashes from other plants.

Data obtained to date from the Ottumwa ash paste tests and ASTM C 311 tests were summarized and combined for analysis. Results are given in Tables 2 and 3 where $\bar{X}$ refers to the arithmetic mean, S refers to the standard deviation, R refers to the range, and n denotes the number of samples.

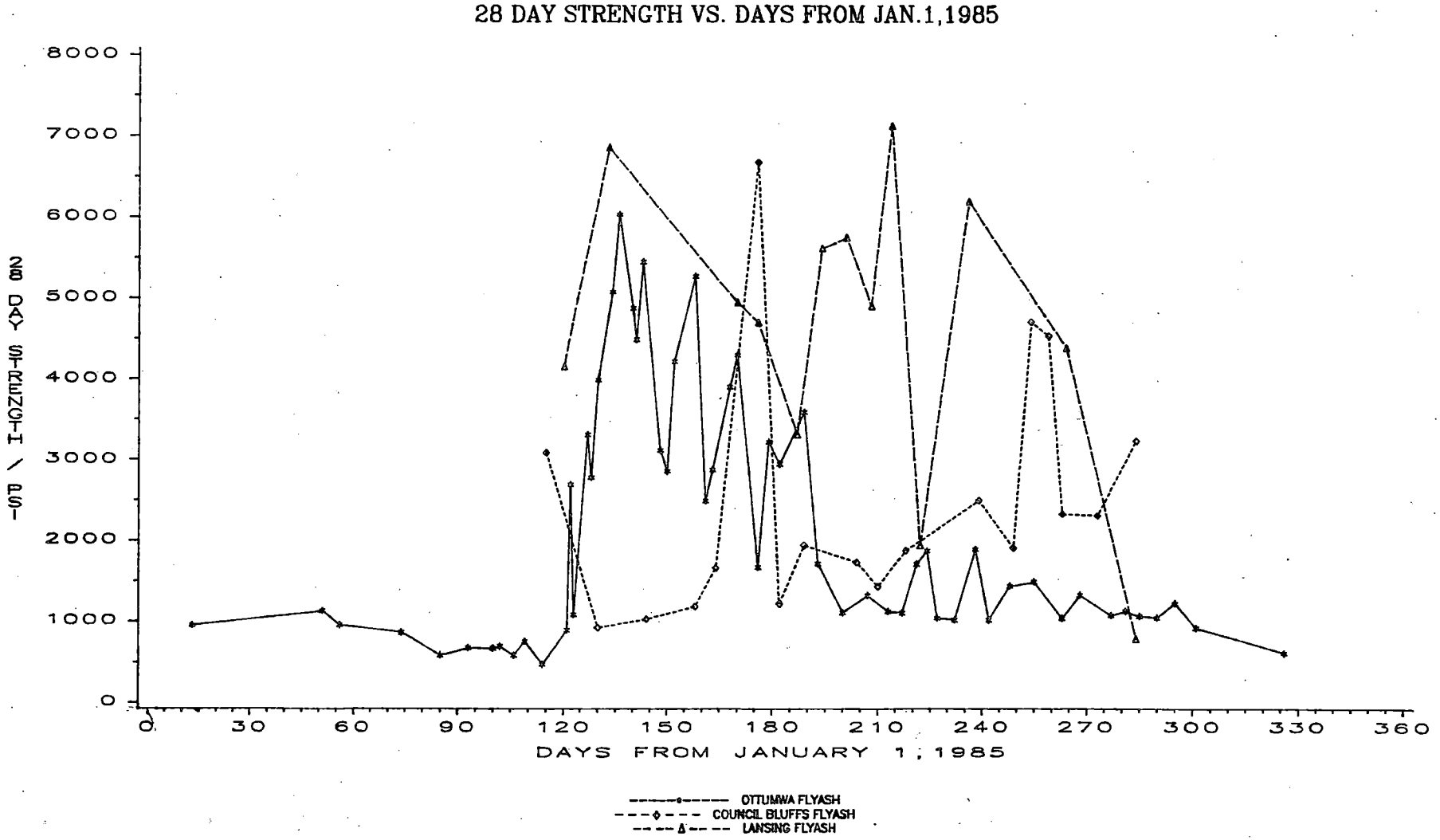

Figure 4. Compressive strength comparison of paste cubes from Ottumwa, Council Bluffs and Lansing fly ash.

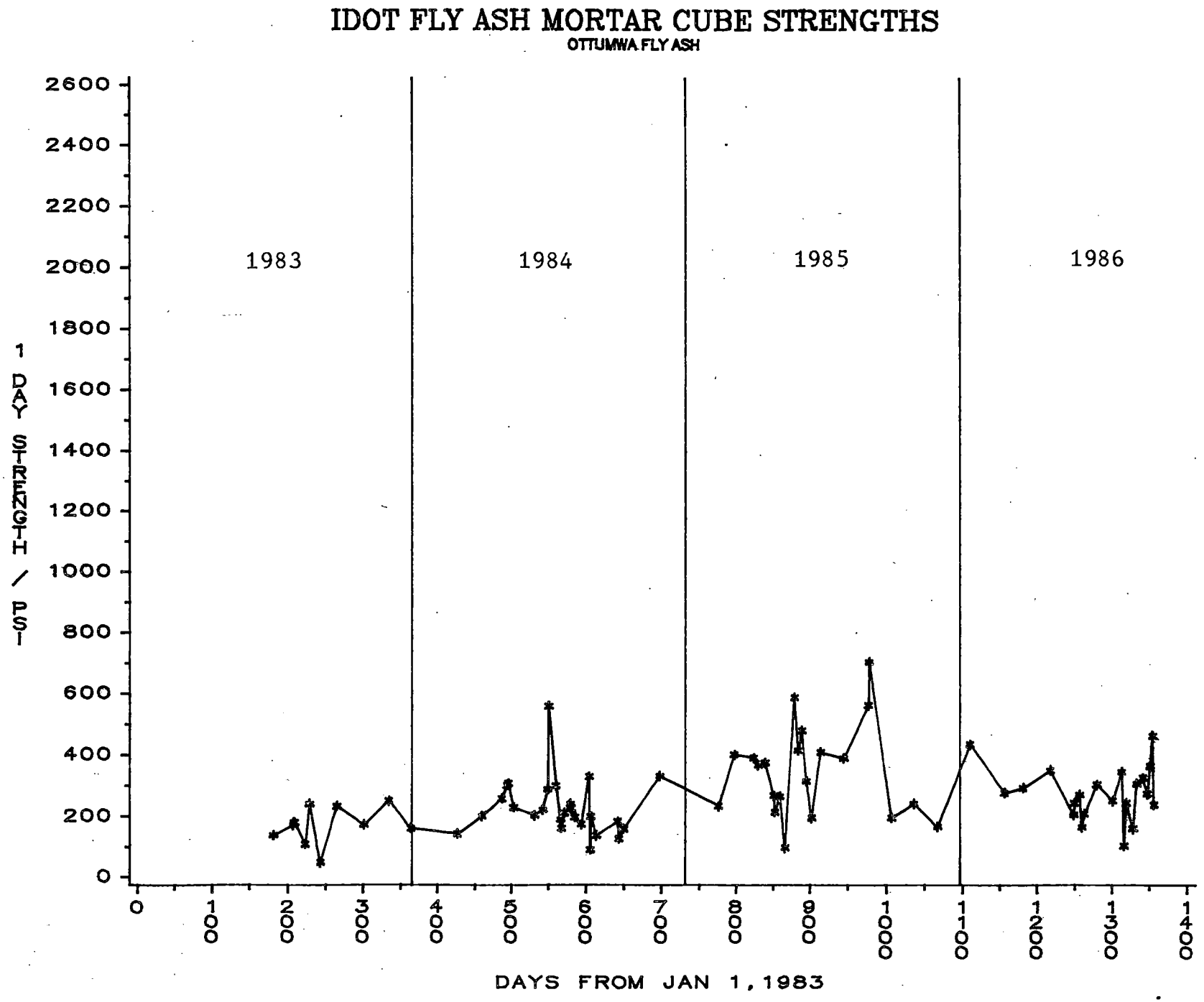

Figure 5. IDOT one day mortar cube strength, Ottumwa fly ash.

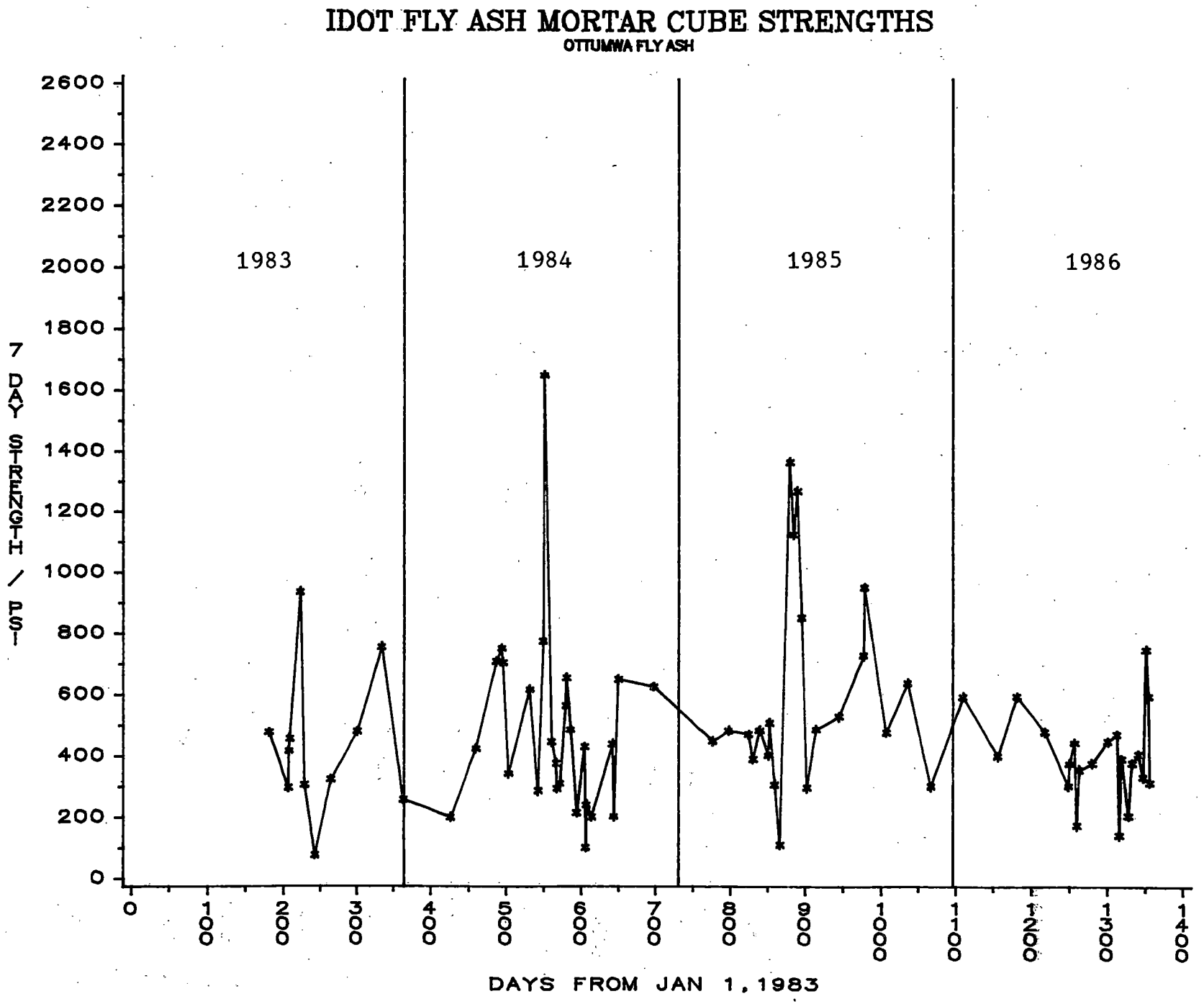

Figure 6. IDOT seven day mortar cube strength, Ottumwa fly ash.

Table 2

Summary of statistics obtained for Ottumwa pastes

Test	$\bar{X}$	S	R	n
Compressive strength (psi)				
4 hour	354	114	531	56
1 day	718	471	2189	51
3 day	1240	915	3597	56
7 day	1571	1145	4407	57
14 day	1796	1299	4773	57
28 day	2083	1511	5571	56
Volume stability (% expansion)				
Air cured	-0.04	0.03	0.06	52
Humid cured	0.00	0.03	0.14	52
Setting time (minutes)				
Initial set	21	8	28	55
Final set	34	15	95	55
Temperature rise				
T (°C)	5.4	1.2	5.5	56
Time to reach peak temp. (min.)	45	15	62	52

Table 3

Summary of statistics obtained from ASTM C 311 tests

	Ottumwa Power Plant Year - 1985 -- n=85		
Test	$\bar{X}$	S	R
Moisture content (%)	0.03	0.02	0.10
Loss on ignition (%)	0.24	0.06	0.24
Fineness (%)	9.83	0.81	3.90
7 day Pozzolan (%)	93.80	5.60	32.00
Autoclave Exp. (%)	0.06	0.02	0.07
Specific Gravity	2.65	0.03	0.16

In reviewing the average, standard deviation and range of test results in Table 2, the variability exhibited for most of the properties is so large that the mean and standard deviation probably cannot be used in design or specification guidelines. By contrast, the data shown in Table 3 for the ASTM C 311 physical properties does not show a large variation. This is further evidence that the ASTM physical tests do not reflect, or give any indication of, the high variability in physical properties of fly ash pastes. Statistical analyses were conducted in an attempt to find a correlation between the data in Table 2 (paste tests) to the data in Table 3 (ASTM physical tests). No correlation coefficients greater than 0.5 were observed from this data.

Correlation coefficients were developed for the fly ash/water paste variables given in Table 2 and are presented in Table 4.

Compressive strengths of fly ash pastes cured for short periods of time (i.e., one to seven days) correlated well with compressive strengths observed for the samples cured for both 14 and 28 days. The best correlation observed for the compressive strength data was between the 7 day and the 28 day strength of the fly ash pastes, which had a correlation coefficient of 0.947. The correlation of the 1 day test to the 28 day test was 0.782. These results indicate that a reasonable estimate characterizing 28 day strength

Table 4

Pearson correlation coefficients for variables listed in Table 2

	Test variable - Compressive Strength					
Test Variable	4 hour	1 day	3 day	7 day	14 day	28 day
Exp. (humid cure)	-0.152	0.637	0.786	0.731	0.751	0.817
Exp. (air cure)	-0.132	-0.389	-0.464	-0.442	-0.465	-0,474
Initial set	-0.130	0.022	0.090	0.104	0.041	-0.045
Final set	-0.258	-0.226	-0.227	-0.291	-0.300	-0.326
△ T	0.640	0.370	0.307	0.229	0.246	0.211
Time to peak	0.196	-0.111	-0.242	-0.229	-0.341	-0.321
Compressive strength						
4 hour	1.0					
1 day	0.321	1.0			symmetric	
3 day	0.143	0.904	1.0			
7 day	0.109	0.800	0.909	1.0		
14 day	0.131	0.767	0.816	0.881	1.0	
28 day	0.076	0.782	0.910	0.947	0.912	1.0

development may be possible from early age strength tests on small paste samples. Figure 7 illustrates typical strength development and volumetric stability curves for paste mixes. From Figure 7 it is seen that strength development is initially quite rapid, but that after about 14 days of moist curing there is little gain in compressive strength.

Volume stability of the humid-cured fly ash pastes correlates fairly well to compressive strength (see Table 4, maximum R = 0.817). Figure 8 depicts results of expansion/shrinkage values versus 28 day strength for the Ottumwa fly ash pastes. Results for the Lansing and Council Bluffs pastes exhibited similar trends. In general, the test specimens with moderate to high compressive strengths

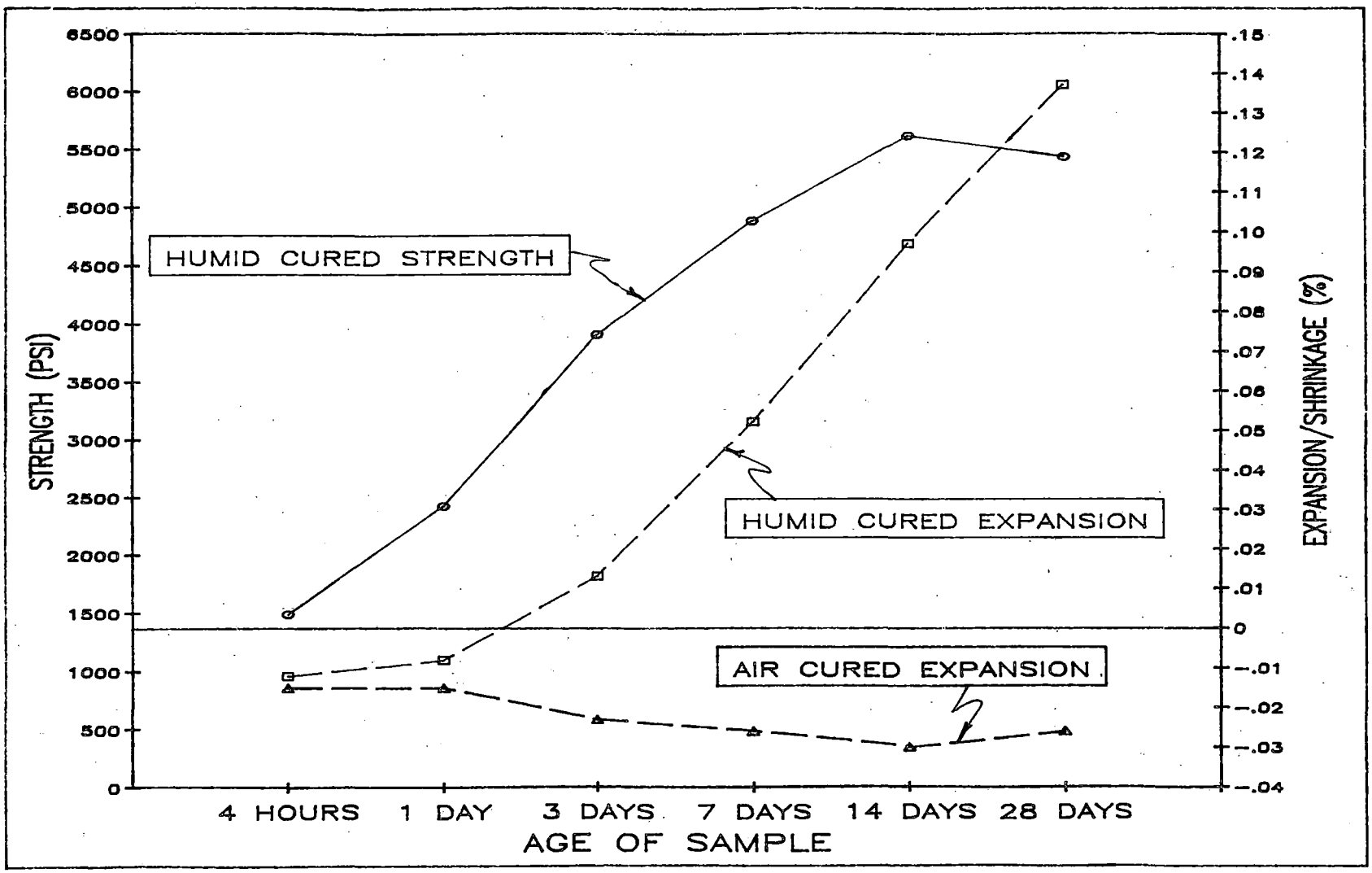

Figure 7. Typical fly ash strength development and volumetric stability curves.

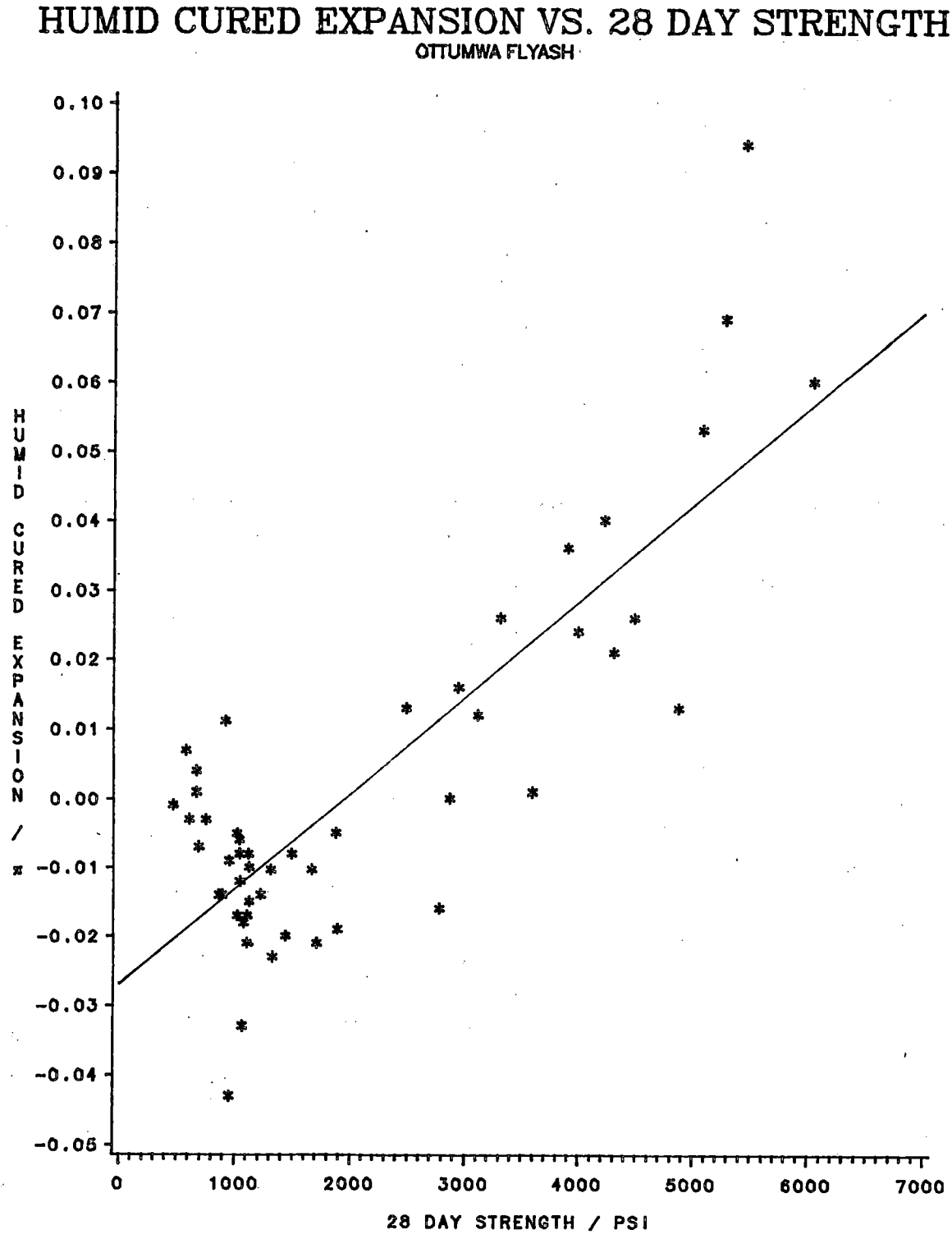

Figure 8. Humid cured expansion versus 28 day strength, Ottumwa fly ash.

exhibited a slight expansion during the 28 day curing period. Specimens that had low compressive strengths displayed a negligible expansion or slight shrinkage. The expansion of the air-cured specimens did not show a strong correlation to compressive strength. In fact, the air-cured specimens showed a slight negative correlation to compressive strength. Typically, the specimens that had the largest expansion when subjected to humid-curing also displayed the greatest drying shrinkage when subjected to air curing. This may suggest that fly ash pastes could be susceptible to severe volume changes during wetting-drying cycles. Many of the air-cured specimens demonstrated modest to severe efflorescence tendencies during the first week of curing. The white powder was carefully scraped from several of the specimens. X-ray diffraction analysis indicated that the powder was sodium sulfate.

Time of set data was highly variable. The average values are very poor estimates of the initial and final set times for a given sample of the Ottumwa fly ash. Several of the samples had a tendency to flash set. In such mixtures final set occurred in less than 15 minutes from the time that water was added to the fly ash. Other samples had final set times of nearly 120 minutes. This large sample to sample variation of setting time makes field utilization of the fly ash difficult. The setting times, however, were quite rapid and

could easily be monitored in the field on a lot by lot basis, if needed, using inexpensive equipment. Also, initial set showed a modest correlation to final set (R = 0.675) so the pastes may only need to be monitored until initial set occurs. Only poor (if any) correlations existed between setting time and the other variables studied in this research.

The temperature rise (ΔT) data showed a correlation to the 4 hour compressive strength data. This correlation may be real, but the temperature rise test should also be dependent on both the specific surface area and the chemical composition of the fly ash. Figure 9 shows the results of 4 hour strength to temperature rise for the Ottumwa, Lansing and Council Bluffs ashes. This data indicates the correlation may hold for ash not only from a given plant, but between ashes from different plants. Further work is continuing in this area to determine if this data can be used as a characterization means.

In summary, the fly ash paste testing conducted to date, using ashes from the Ottumwa, Lansing and Council Bluffs power plants, has proven that there is a significant variation in physical properties of hydrated pastes that is not evidenced in any form from current ASTM chemical and physical testing. These variations appear to be cyclical and may be a function of (1) plant maintenance schedules,

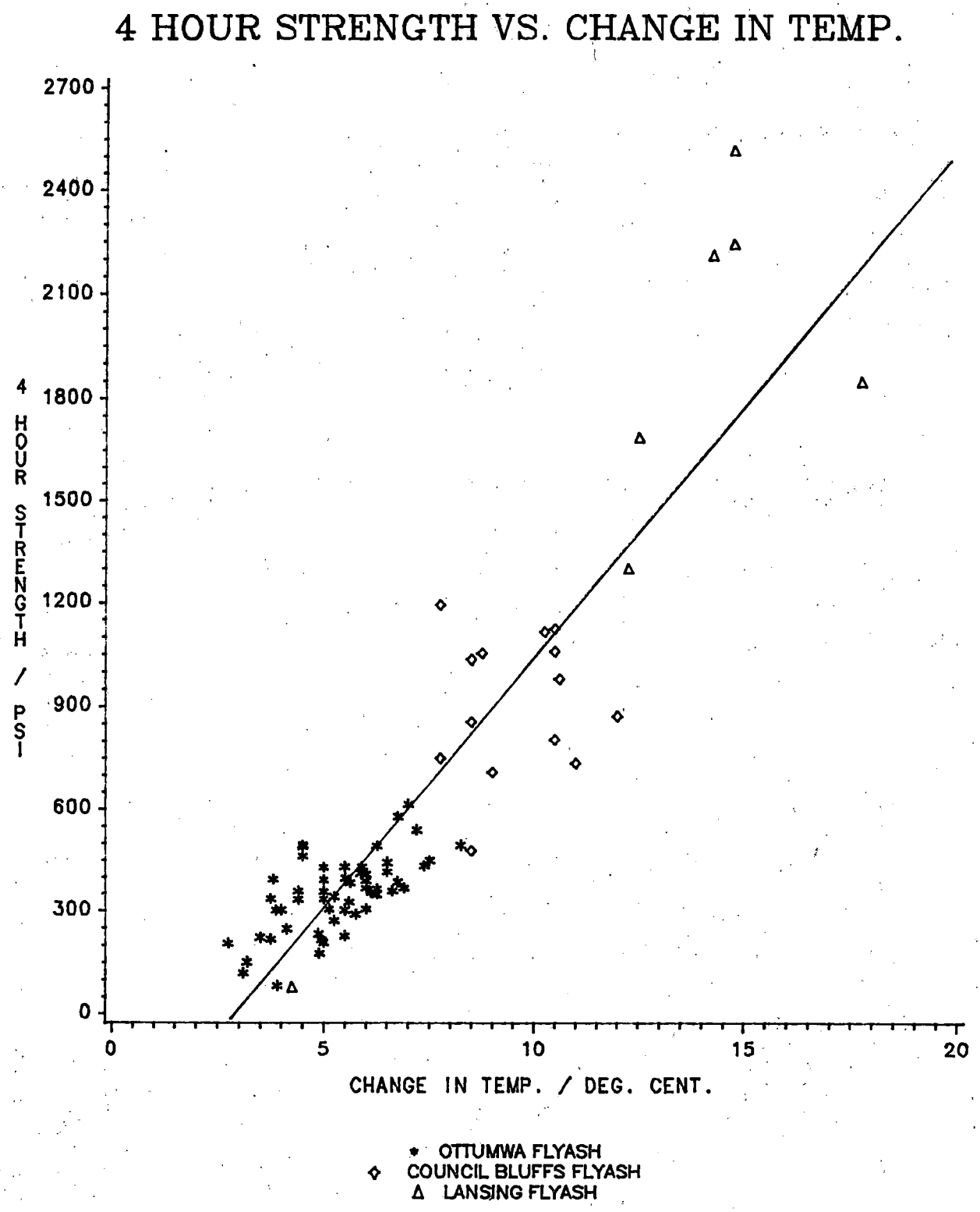

Figure 9. Four hour paste strength versus temperature rise.

(2) plant operating levels, or (3) sodium carbonate coal treatment processes (time and amount), or a combination of these. Research efforts next year will address these factors.

Quantitative X-ray Fluorescence

Quantitative x-ray fluorescence (QXRF) studies were initiated in order to provide a basis for understanding the relationship between the chemical composition of a fly ash and the highly variable physical properties exhibited by the fly ash/water pastes. QXRF analysis was performed on 22 samples of the Ottumwa fly ash. The samples were selected to represent a cross section of low strength to high strength pastes (see Figure 3). Table 5 summarizes the test results. This data reveals a very interesting trend with regard to bulk Na_2O content. Figure 10 depicts the results of Na_2O content of samples of the Ottumwa ash tested and plotted on the same graph as 7 day paste strength. It can be seen that the percent Na_2O curve is nearly a mirror image of the strength curve, and also exhibits a cyclical trend. This may be related to the use of sodium carbonate treatment of the raw coal and will be further investigated during the next year. The Na_2O content is very important because the total alkali content will dominate the pore solution equilibria in fly ash/water pastes. As the sodium ion concentration increases in the pore solution it would be expected that the

Table 5

QXRF Results for Ottumwa Fly Ash - 1985

		Oxide (wt %)												
Sample	Day	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MnO	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	BaO	SrO
OTT011385	13	34.3	18.8	5.94	2.39	0.03	23.3	4.21	0.39	2.34	1.13	1.50	0.70	0.45
OTT022085	51	32.0	18.6	5.38	2.74	0.03	24.5	4.71	0.36	2.42	1.10	1.10	0.63	0.42
OTT031585	74	32.0	18.8	5.36	2.75	0.03	24.0	4.52	0.40	2.70	1.12	1.19	0.64	0.42
OTT032685	85	32.0	18.7	5.21	2.44	0.02	23.1	4.47	0.43	2.67	1.11	2.15	0.84	0.52
OTT040385	92	30.6	17.5	5.0	2.90	-	24.4	4.95	0.40	3.12	1.32	2.58	-	-
OTT041085	99	29.4	17.8	4.9	2.97	-	24.5	4.83	0.39	3.12	1.35	1.93	-	-
OTT041685	105	32.2	17.6	5.0	4.01	-	24.0	4.78	0.41	2.96	1.35	1.84	-	-
OTT050185	120	33.8	18.2	5.0	2.00	-	23.7	4.72	0.44	1.99	1.36	1.83	-	-
OTT050285	121	34.2	18.2	5.2	1.67	-	23.8	4.62	0.44	1.77	1.39	1.80	-	-
OTT050385	122	34.0	18.4	5.2	1.83	-	23.8	4.76	0.44	1.86	1.39	1.82	-	-
OTT050785	127	32.2	18.6	6.53	2.37	0.03	25.0	4.36	0.33	1.75	1.12	1.40	0.66	0.45
OTT050885	128	34.4	18.4	6.1	2.36	-	25.4	4.93	0.37	2.08	1.48	1.50	-	-
OTT051485	134	33.3	18.3	6.0	2.50	-	25.6	4.85	0.34	2.16	1.48	1.72	-	-
OTT051685	136	31.1	18.6	6.51	2.30	0.04	25.6	4.35	0.30	1.72	1.10	1.77	0.70	0.48
OTT051985	139	31.2	18.9	6.60	2.48	0.04	25.8	4.33	0.32	1.84	1.11	1.43	0.67	0.45
OTT052085	140	31.7	18.1	6.0	2.16	-	25.7	4.84	0.33	1.94	1.43	1.95	-	-
OTT052385	143	29.2	17.8	6.0	2.34	-	26.3	4.88	0.31	1.89	1.39	2.23	-	-
OTT052885	148	30.6	17.9	6.0	2.31	-	26.0	4.96	0.33	1.89	1.42	2.06	-	-
OTT061085	161	33.2	19.0	6.16	2.07	0.03	23.2	4.23	0.36	1.64	1.06	2.00	0.79	0.58
OTT071985	200	31.4	19.1	6.15	2.66	0.03	24.5	4.28	0.37	2.21	1.10	1.17	0.64	0.42
OTT072685	207	30.6	19.4	6.33	2.55	0.04	25.2	4.37	0.36	2.06	1.12	1.07	0.62	0.42
OTT080185	213	30.8	18.9	5.96	2.46	0.03	25.0	4.57	0.37	2.05	1.09	1.44	0.71	0.46

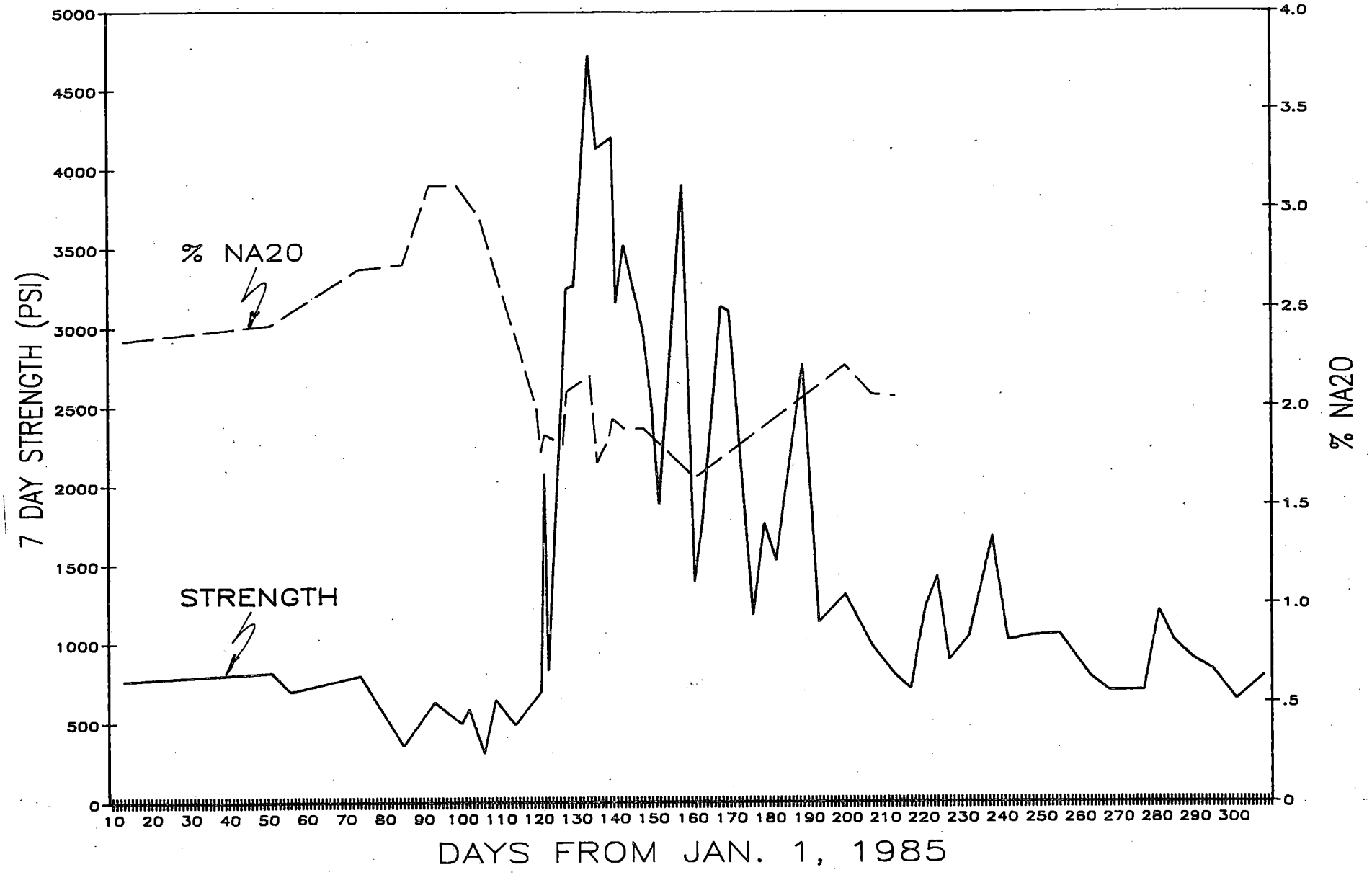

Figure 10. Ottumwa fly ash paste 7 day strength comparison to raw fly ash Na_2O content.

calcium ion concentration would decrease due to the common ion effect. As the calcium ion concentration decreases, it would be expected that the stability of ettringite formation would be increased because the equivalent sulphate to calcium ion ratio would increase drastically. It is premature to conclude that only the Na_2O content influences the strength behavior, however, it may be a principal contributor.

It is also noted from the data in Table 5 that there are relatively large concentrations of barium and strontium in the Ottumwa ash. These two elements can also influence the pore solution equilibria of fly ash pastes because both can form nearly insoluble sulfates. These sulfates are then not available for the formation of strength producing cementitious reaction products; therefore, the amount of analytical SO_3 measured in bulk fly ash must be reduced to account for the insoluble compounds produced. For the Ottumwa ash this correction would amount to a reduction of about 0.7 percent of the bulk analytical SO_3 content.

Quantitative X-ray Diffraction

Sixteen of the raw Ottumwa fly ash samples were analyzed by x-ray diffraction. Samples were selected to represent the range of low to high paste strengths noted on Figure 3. These analyses were conducted in an attempt to identify the various compounds present in the ashes and/or changes in their relative amounts. These data might help to explain the

high variability in physical properties of the pastes.

A Siemens D 500 x-ray diffractometer was used for all analyses. This unit is fully automated by a PDP 11/23 computer system. Samples were side loaded into plexiglass holders, and scanned from 2 to 70 degrees 2-theta at a rate of about 1 degree per minute.

In general, all of the samples contained quartz, anhydrite, lime, periclase and a mineral similar to tricalcium aluminate. Some of the samples also contained mullite and tetracalcium trialuminate sulphate.

Quantitative x-ray diffraction (QXRD) analysis of fly ash is a complex problem due to (1) small amounts of the compounds present, (2) numerous compounds in the ash with peak overlapping, (3) the presence of the glassy phase, and (4) isomorphous substitution. As of this writing quantitative evaluation of the amounts of compounds present are, at best, estimates only; nevertheless, it is necessary to define the cause(s) of the paste variations and to provide input to a rational characterization method. Table 6 summarizes the results of QXRD on 10 raw Ottumwa fly ash samples; again, traversing the low to high strength paste region shown on Figure 3. The values shown on Table 6 are expressed relative to the concentrations of the various compounds present in the OTT051685 sample. From this data, it is noted that the variation in relative amount of

Table 6

QXRD results for Ottumwa fly ash

Sample	Day	Concentrations (wt %) relative to OTT051686 compounds				
		SiO_2	$CaSO_4$	CaO	MgO	C_3A*
OTT011385	13	1.23	1.10	0.71	0.75	0.49
OTT022085	51	0.58	1.19	1.39	0.95	0.57
OTT031585	74	0.75	1.13	1.40	0.81	0.71
OTT032685	85	0.79	1.01	0.82	0.79	0.58
OTT050785	127	0.85	1.05	1.17	0.83	0.91
OTT051685	136	1.00	1.00	1.00	1.00	1.00
OTT061085	161	0.85	0.83	0.86	1.01	0.71
OTT071985	200	0.95	1.32	1.31	1.03	0.66
OTT072685	207	1.18	1.12	0.94	0.94	0.69
OTT080185	213	0.86	0.88	-	0.89	0.88

*ratios based on peak height only

tricalcium aluminate (C_3A) roughly corresponds to variation in paste compressive strength shown on Figure 3. Obviously the cause of the variation in paste properties is more complicated than simply C_3A content. As previously noted, the Na_2O and SO_3 contents of the ashes are also believed to be influencing the system behavior. Further work is continuing in this area.

Differential Thermal Analysis

It had been thought that differential thermal analysis (DTA) data might provide some additional insight on the properties of the compounds and the glassy phase present in fly ash. Several DTA scans were conducted on the raw Ottumwa fly ash

up to a temperature of 1150 degrees centigrade. There were no significant transitions until an exothermic peak was observed at about 910 degrees centigrade. This was probably the recrystallization of gehlenite from the glassy phase. An endothermic peak onsetting at about 1050 degrees centigrade was probably indicative of partial melting. Further work in this area will be directed at higher operating temperatures using platinum crucibles and DTA testing of fractionated fly ash samples.

SUMMARY AND CONCLUSION

The results of the first years research effort, directed toward development of a rational characterization method for Iowa fly ashes, are briefly summarized as follows.

1. The results of ASTM C 618 physical and chemical testing (to classify and characterize fly ash for use in concrete) show little variation with time, irrespective of ash source.

2. There is no significant correlation of ASTM C 618 physical and chemical test results to the highly variable physical properties (i.e., compressive strength development, volumetric stability, heat evolution or setting time) exhibited by paste mixes of ashes from various sources.

3. The variation in paste physical properties appears to be cyclical, on a yearly basis, with the greatest variation and increased strength observed during peak summer loading periods. The variation may be linked to plant maintenance schedules and to the timing and amount of sodium carbonate coal treatments. This will be investigated thoroughly during the next year.

4. Chemical and physical testing indicates that Na_2O, SO_4, and C_3A contents of the ashes could be causing pore solution equilibria changes that are influencing cementitious reaction product development. This could in turn cause significant variability in the physical properties of the pastes. Research is continuing in this area.

5. Fly ash paste mixes exhibited significant differences in shrinkage/expansion characteristics depending on curing method (air or humid). This could indicate a potential volumetric stability problem in field use of the ashes. It is being investigated in more depth.

6. The current method of grab sampling each 20 ton truckload of fly ash and combining 20 of these to form a composite sample representing 400 tons of fly ash could be masking larger daily variations in ash paste properties. The sampling program for the next year will address this potential problem.

It is evident from this years research that the variability of paste properties exhibited by ashes from all the sources is high and can occur over a short span of time. It appears that a characterization method must, therefore, be capable of quickly (one day or less) assessing the physical properties in the field. Further research and method development will be directed toward this objective.

ACKNOWLEDGEMENT

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REFERENCES

1. Schlorholtz, S., Bergeson, K., and Demirel, T. "Variability and Trends in Iowa Fly Ashes," presented to the 1986 Fall meeting, Materials Research Society, Boston, Massachusetts, December 1, 1986. (to be published)

2. Lee, C., Schlorholtz, S., and Demirel, T. Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal II, Materials Research Society Symposium, Vol. 65, edited by McCarthy, Glasser and Roy (Materials Research Society), Pittsburg, 1986, pp 125-130.

Table 1

Summary of Results of ASTM C 618 Testing of Fly Ashes from 1983 to 1986.

Council Bluffs Power Plant

Year →	1983 n = 4			1984 n = 7			1985 n = 9		
Test	$\bar{X}$	S	R	$\bar{X}$	S	R	$\bar{X}$	S	R
Moisture content	0.07	0.02	0.03	0.06	0.03	0.07	0.09	0.06	0.20
Loss on Ignition	0.32	0.13	0.29	0.45	0.08	0.22	0.47	0.14	0.42
Fineness	10.82	3.20	6.86	11.73	2.05	6.77	13.30	3.13	9.90
7 Day Pozzolan	Not Determined			89.7	6.4	19.0	86.7	4.6	12.0
Autoclave Exp.	0.14	0.01	0.03	0.06	0.01	0.04	0.11	0.03	0.09
Specific Gravity	2.71	0.03	0.06	2.65	0.05	0.11	2.71	0.03	0.10
28-Day Pozzolan	98.8	4.0	9.0	100.9	8.3	24.0	87.9	3.7	10.0
H_2O Required	91.5	5.3	10.0	90.3	0.76	2.0	88.8	1.4	5.0
SiO_2	31.48	0.65	1.51	33.64	1.67	5.24	30.81	1.64	4.50
Al_2O_3	16.90	0.26	0.55	17.15	0.57	1.67	15.82	0.62	1.80
Fe_2O_3	5.15	0.16	0.33	5.06	0.24	0.77	5.40	0.45	1.37
SO_3	3.06	0.30	0.64	2.77	0.30	0.81	3.78	0.50	1.29
CaO	27.90	0.56	1.36	26.83	0.86	2.19	28.12	0.42	1.10
MgO	6.65	0.16	0.35	5.67	0.21	0.60	5.80	0.49	1.45
P_2O_5	0.87	0.14	0.78*	1.24	0.18	0.54	1.00	0.18	0.65
K_2O	0.33	0.04	0.08	0.34	0.04	0.13	0.28	0.04	0.11
Na_2O	1.78	0.08	0.19	1.98	0.16	0.44	1.91	0.16	0.49
TiO_2	1.36	0.04	0.08*	1.33	0.07	0.22	1.24	0.14	0.41
Avail. Alk.	1.31	0.09	0.22	1.28	0.16	0.52	1.34	0.15	0.42

*Denotes n = 3

Table 1 (Continued)

Lansing Power Plant

Year →	1983 n = 4			1984 n = 4			1985 n = 7		
Test	$\bar{X}$	S	R	$\bar{X}$	S	R	$\bar{X}$	S	R
Moisture Content	0.04	0.03	0.06	0.04	0.04	0.07	0.05	0.05	0.14
Loss on Ignition	0.44	0.27	0.56	0.29	0.05	0.11	0.47	0.18	0.56
Fineness	12.95	2.35	5.23	11.17	2.82	6.18	12.77	1.92	6.80
7-Day Pozzolan	Not Required			90.3	2.2	5.0	90.0	5.1	13.0
Autoclave Exp.	0.11	0.02	0.04	0.07	0.01	0.02	0.10	0.03	0.08
Specific Gravity	2.77	0.04	0.09	2.78	0.02	0.05	2.79	0.02	0.07
28-Day Pozzolan	85.8	7.7	18.0	91.2	8.0	19.0	86.9	5.1	16.0
H_2O Required	95.5	5.4	12.0	90.0	0.0	0.0	89.4	1.0	3.0
SiO_2	35.72	3.68	7.70	34.32	3.19	7.37	31.50	1.41	4.00
Al_2O_3	16.72	0.66	1.60	15.58	0.17	0.38	15.53	0.46	1.40
Fe_2O_3	5.54	0.22	0.52	5.68	0.42	0.97	5.94	0.38	1.20
SO_3	3.66	0.68	1.63	4.29	0.70	1.52	4.35	0.36	1.03
CaO	26.72	0.68	1.44	26.82	1.07	2.39	27.66	0.64	1.60
MgO	6.63	0.51	1.16	6.06	0.37	0.87	5.77	0.30	0.89
P_2O_5	1.00	0.30	0.57*	0.84	0.08	0.19	0.86	0.19	0.64
K_2O	0.38	0.02	0.04	0.40	0.12	0.27	0.29	0.04	0.10
Na_2O	2.05	0.20	0.45	1.88	0.05	0.10	2.06	0.24	0.71
TiO_2	1.29	0.03	0.06*	1.20	0.04	0.07	1.20	0.10	0.33
Avail. Alk.	1.42	0.11	0.25	1.33	0.11	0.24	1.44	0.22	0.57

*Denotes n = 3

Table I (Continued)

Neal #4 Power Plant

Year →	1983 n = 4			1984 n = 6			1985[a] n = 15		
Test	$\bar{X}$	S	R	$\bar{X}$	S	R	$\bar{X}$	S	R
Moisture Content	0.02	0.01	0.03	0.03	0.03	0.07	0.03	0.02	0.06
Loss on Ignition	0.17	0.01	0.03	0.31	0.06	0.14	0.31	0.04	0.14
Fineness	7.49	2.56	5.79	11.57	0.69	2.06	11.42	2.20	7.10
7-Day Pozzolan	Not Required			88.4	6.1	16.0	92.7	5.1	20.0
Autoclave Exp.	0.08	0.01	0.02	0.06	0.02	0.05	0.07	0.02	0.07
Specific Gravity	2.69	0.02	0.04	2.66	0.04	0.11	2.59	0.08	0.28
28-Day Pozzolan	104.2	8.8	19.0	90.3	5.2	14.0	95.3	6.8	25.0
H_2O Required	88.2	0.5	1.0	91.8	4.0	10.0	88.5	1.0	4.0
SiO_2	35.20	0.97	2.19	33.63	1.00	2.74	35.23	2.52	9.98
Al_2O_3	15.68	0.25	0.58	15.69	0.55	1.61	16.24	0.91	3.11
Fe_2O_3	6.20	0.13	0.24	5.83	0.26	0.68	5.59	0.50	1.67
SO_3	3.33	0.28	0.60	3.82	0.60	1.36	3.25	0.74	2.56
CaO	25.89	0.41	0.90	25.88	0.57	1.71	25.45	1.62	4.89
MgO	6.04	0.22	0.50	5.81	0.22	0.52	5.65	0.41	1.34
P_2O_5	0.76	0.05	0.09*	0.97	0.20	0.51	0.99	0.19	0.74
K_2O	0.29	0.05	0.12	0.30	0.03	0.08	0.32	0.07	0.22
Na_2O	2.08	0.12	0.29	2.54	0.19	0.43	2.20	0.23	0.78
TiO_2	1.02	0.02	0.04	1.04	0.06	0.16	1.06	0.07	0.11
Avail. Alk.	1.46	0.08	0.18*	1.57	0.16	0.39	1.39	0.27	0.89

[a]Denotes that two different coal sources were used in 1985.

*Denotes n = 3

TABLE 1 (Continued)

Ottumwa Power Plant

Year →	1983 n = 8			1984 n = 17			1985 n = 17		
Test	$\bar{X}$	S	R	$\bar{X}$	S	R	$\bar{X}$	S	R
Moisture Content	0.04	0.02	0.05	0.03	0.01	0.05	0.03	0.02	0.06
Loss on Ignition	0.24	0.05	0.14	0.26	0.05	0.21	0.25	0.06	0.21
Fineness	10.22	0.32	0.94	10.41	0.75	2.74	9.99	0.69	2.50
7-Day Pozzolan	Not Required			90.2	6.3	23.0	91.9	4.0	16.0
Autoclave Exp.	0.05	0.02	0.06	0.03	0.01	0.04	0.06	0.02	0.05
Specific Gravity	2.61	0.02	0.06	2.60	0.03	0.12	2.65	0.03	0.11
2 -Day Pozzolan	103.1	10.6	30.0	97.6	5.7	20.0	94.2	6.3	23.0
H_2O Required	89.1	3.4	10.0	90.2	0.8	3.0	86.8	1.9	9.0
SiO_2	34.48	1.49	4.86	35.33	1.42	5.05	32.23	1.64	6.48
Al_2O_3	19.98	0.41	1.20	18.36	0.35	1.60	18.33	0.34	1.29
Fe_2O_3	5.23	0.14	0.44	5.19	0.16	0.63	5.44	0.40	1.28
SO_3	1.67	0.22	0.65	2.16	0.37	1.32	2.56	0.44	1.76
CaO	24.72	0.68	1.89	23.77	0.70	2.17	25.11	0.54	2.03
MgO	4.94	0.19	0.57	4.63	0.16	0.57	4.92	0.13	0.54
P_2O_5	1.41	0.30	0.92*	1.80	0.23	0.84	1.59	0.38	1.20
K_2O	0.40	0.03	0.09	0.40	0.04	0.12	0.38	0.03	0.09
Na_2O	1.96	0.24	0.67	2.58	0.16	0.55	2.13	0.52	1.95
TiO_2	1.47	0.05	0.16*	1.37	0.05	0.16	1.42	0.04	0.13
Avail. Alk.	1.41	0.18	0.59	1.54	0.30	0.84	1.54	0.33	1.32

*Denotes n = 7

Table II

Summary of Physical Testing of Fly Ash

Council Bluffs Power Plant

Year →	1984 n = 27			1985 n = 24		
Test	$\bar{X}$	S	R	$\bar{X}$	S	R
Moisture Content	0.05	0.05	0.22	0.13	0.14	0.59
Loss on Ignition	0.46	0.12	0.45	0.48	0.29	1.35
Fineness	12.56	1.46	5.91	12.55	2.37	10.50
7-Day Pozzolan	91.5	6.8	29.0	88.6	5.2	22.0
Autoclave Exp.	0.07	0.02	0.07	0.10	0.02	0.08
Specific Gravity	2.65	0.05	0.19	2.71	0.03	0.14

Lansing Power Plant

Year →	1984 n = 13			1985 n = 15		
Test	$\bar{X}$	S	R	$\bar{X}$	S	R
Moisture Content	0.06	0.04	0.14	0.05	0.03	0.14
Loss on Ignition	0.27	0.08	0.29	0.48	0.14	0.50
Fineness	9.46	1.18	3.86	12.18	1.66	5.80
7-Day Pozzolan	87.5	5.9	19.0	86.8	4.2	15.0
Autoclave Exp.	0.07	0.02	0.06	0.11	0.02	0.09
Specific Gravity	2.78	0.03	0.09	2.79	0.03	0.10

Table 11 (Continued)

Neal #4 Power Plant

Year →	1984 n = 14			1985* n = 54		
Test	$\bar{X}$	S	R	$\bar{X}$	S	R
Moisture Content	0.03	0.02	0.08	0.04	0.03	0.16
Loss on Ignition	0.30	0.06	0.20	0.31	0.07	0.31
Fineness	11.30	1.56	4.97	11.32	2.14	8.30
7-Day Pozzolan	87.6	5.0	20.0	92.2	6.2	25.0
Autoclave Exp.	0.07	0.01	0.04	0.07	0.02	0.08
Specific Gravity	2.64	0.03	0.11	2.59	0.08	0.34

Ottumwa Power Plant

Year →	1983 n = 39			1984 n = 78			1985 n = 85		
Test	$\bar{X}$	S	R	$\bar{X}$	S	R	$\bar{X}$	S	R
Moisture Content	0.06	0.03	0.11	0.02	0.01	0.05	0.03	0.02	0.10
Loss on Ignition	0.23	0.08	0.44	0.24	0.06	0.31	0.24	0.06	0.24
Fineness	10.39	0.95	3.80	10.53	1.07	5.06	9.83	0.81	3.90
7-Day Pozzolan	Not Required			92.1	7.9	55.0	93.8	5.6	32.0
Autoclave Exp.	0.05	0.02	0.08	0.03	0.01	0.05	0.06	0.02	0.07
Specific Gravity	2.61	0.04	0.17	2.59	0.04	0.21	2.65	0.03	0.16

*Two different coal sources were used in 1985.

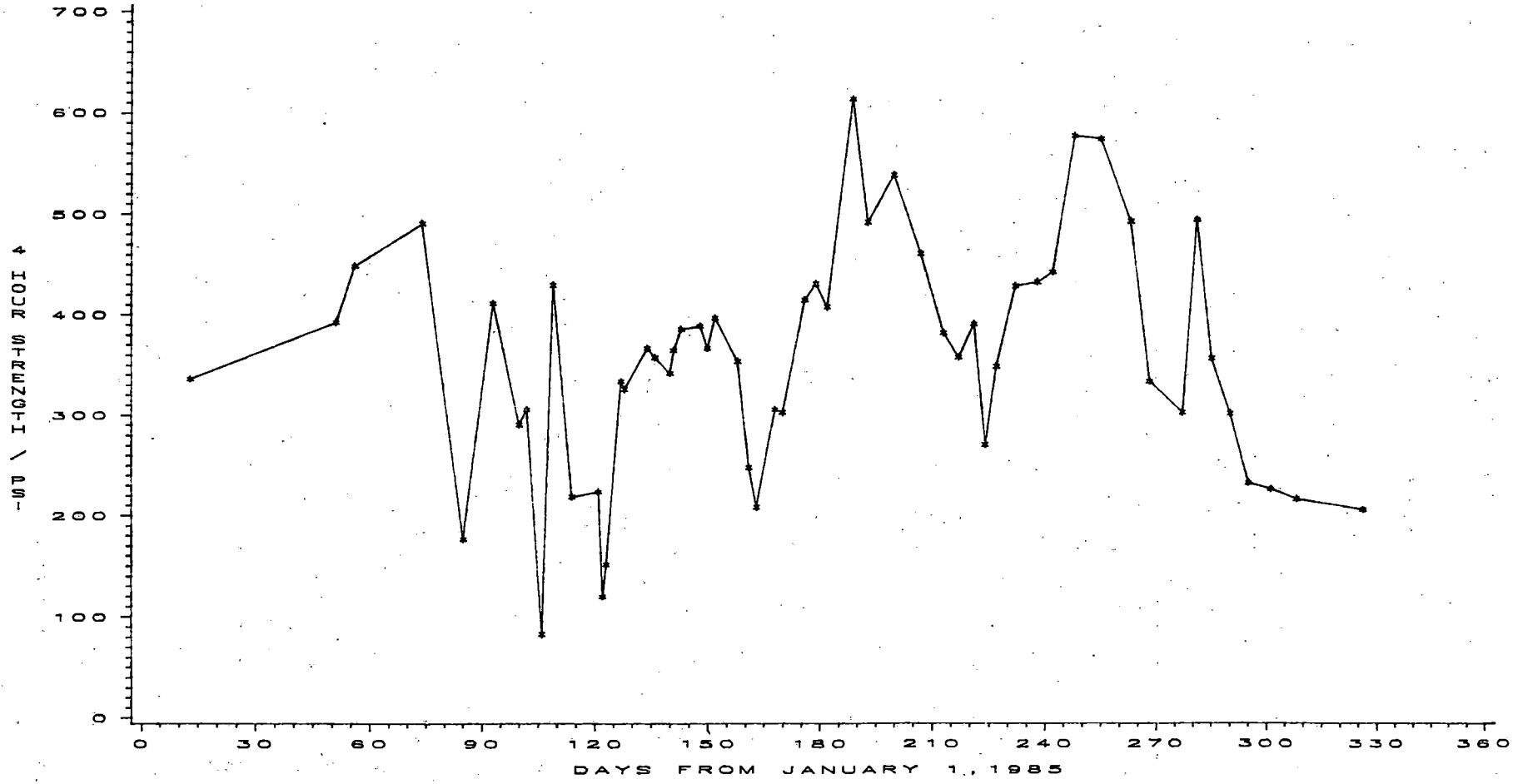
Table III

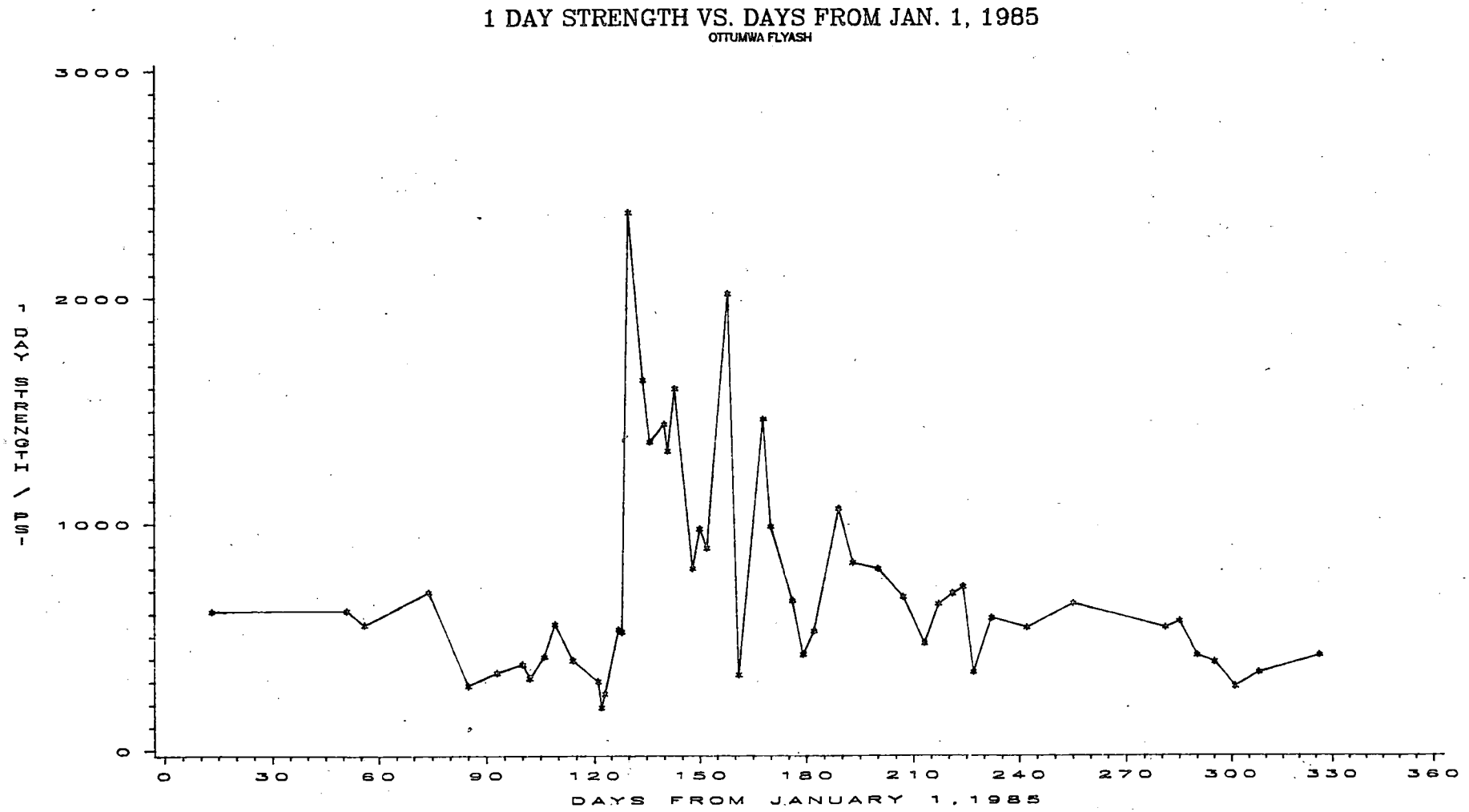
Type I Portland Cements used for pozzolanic activity testing

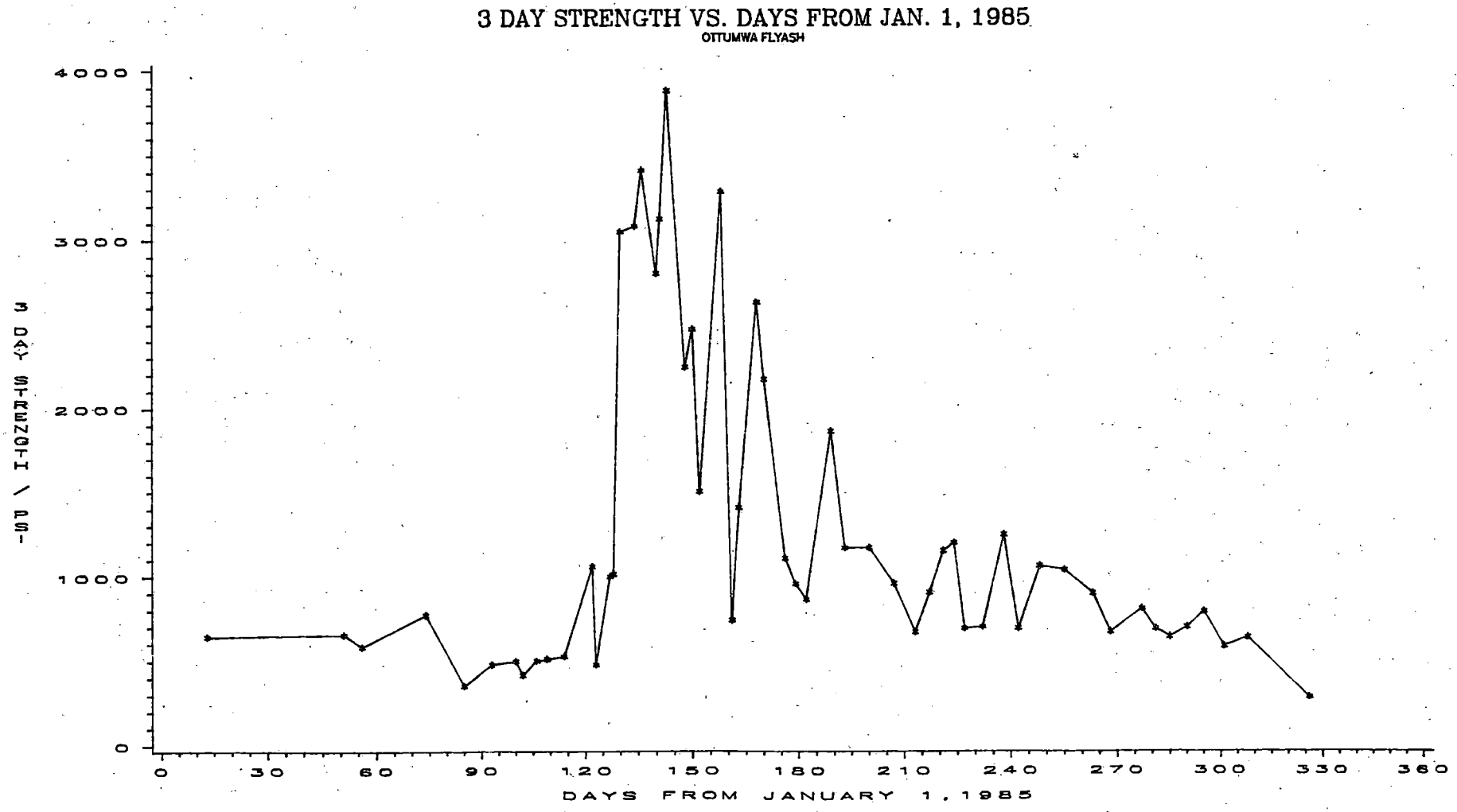
Year	1983	1984			1985		
Oxide	wt%	wt%			wt%		
		A	B	AVG.	A	B	AVG.
CaO	63.0	62.8	62.4	62.6	63.9	63.3	63.6
SiO_2	21.3	21.9	22.2	22.0	21.7	22.3	22.0
Al_2O_3	4.29	4.03	4.32	4.18	4.32	4.50	4.41
Fe_2O_3	3.01	2.97	1.62	2.29	1.64	1.70	1.67
SO_3	2.65	2.37	2.71	2.54	2.57	2.69	2.63
MgO	2.32	2.58	2.23	2.40	3.03	2.63	2.83
K_2O	0.57	0.42	0.57	0.50	0.48	0.59	0.54
Na_2O	0.16	0.26	0.36	0.31	0.28	0.26	0.27
TiO_2	0.22	0.24	0.23	0.24	0.23	0.24	0.24
Bogue Composition (calculated from ASTM C 150)							
C_3S	54			49			52
C_2S	20			26			24
C_3A	6			7			9
C_4AF	9			7			5
Average Compressive Strength (psi)							
7D	N/A			4700			4800
28D	5500			6000			6100

4 HOUR STRENGTH VS. DAYS FROM JAN. 1, 1985

OTTUMWA FLYASH

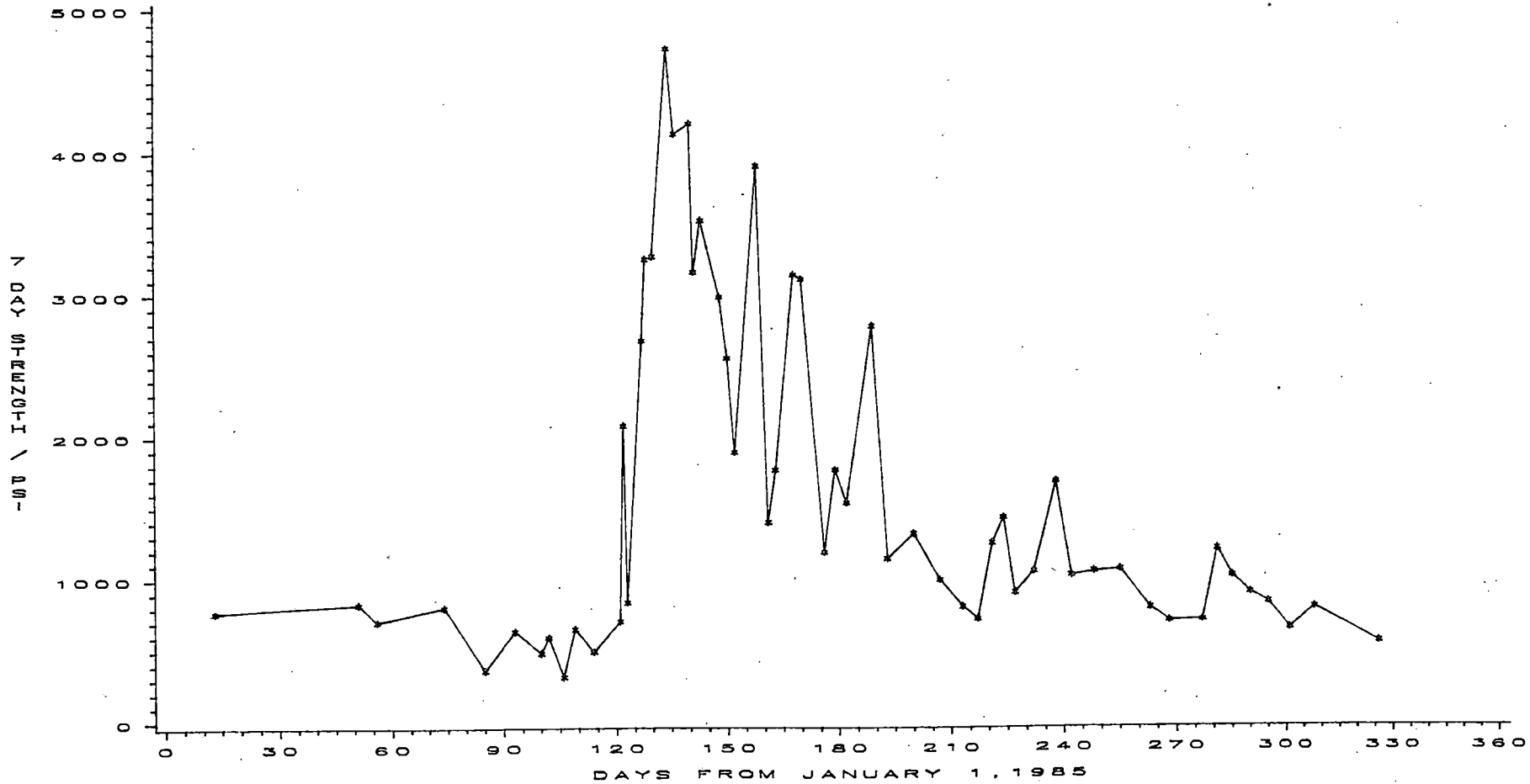



1 DAY STRENGTH VS. DAYS FROM JAN. 1, 1985
OTTUMWA FLYASH
1 DAY STRENGTH \ PSI
3000
2000
1000
0
0
30
60
90
120
150
180
210
240
270
300
330
360
DAYS FROM JANUARY 1, 1985


3 DAY STRENGTH VS. DAYS FROM JAN. 1, 1985
OTTUMWA FLYASH
3 DAY STRENGTH \ PS-
4000
3000
2000
1000
0
0
30
60
90
120
150
180
210
240
270
300
330
360
DAYS FROM JANUARY 1, 1985

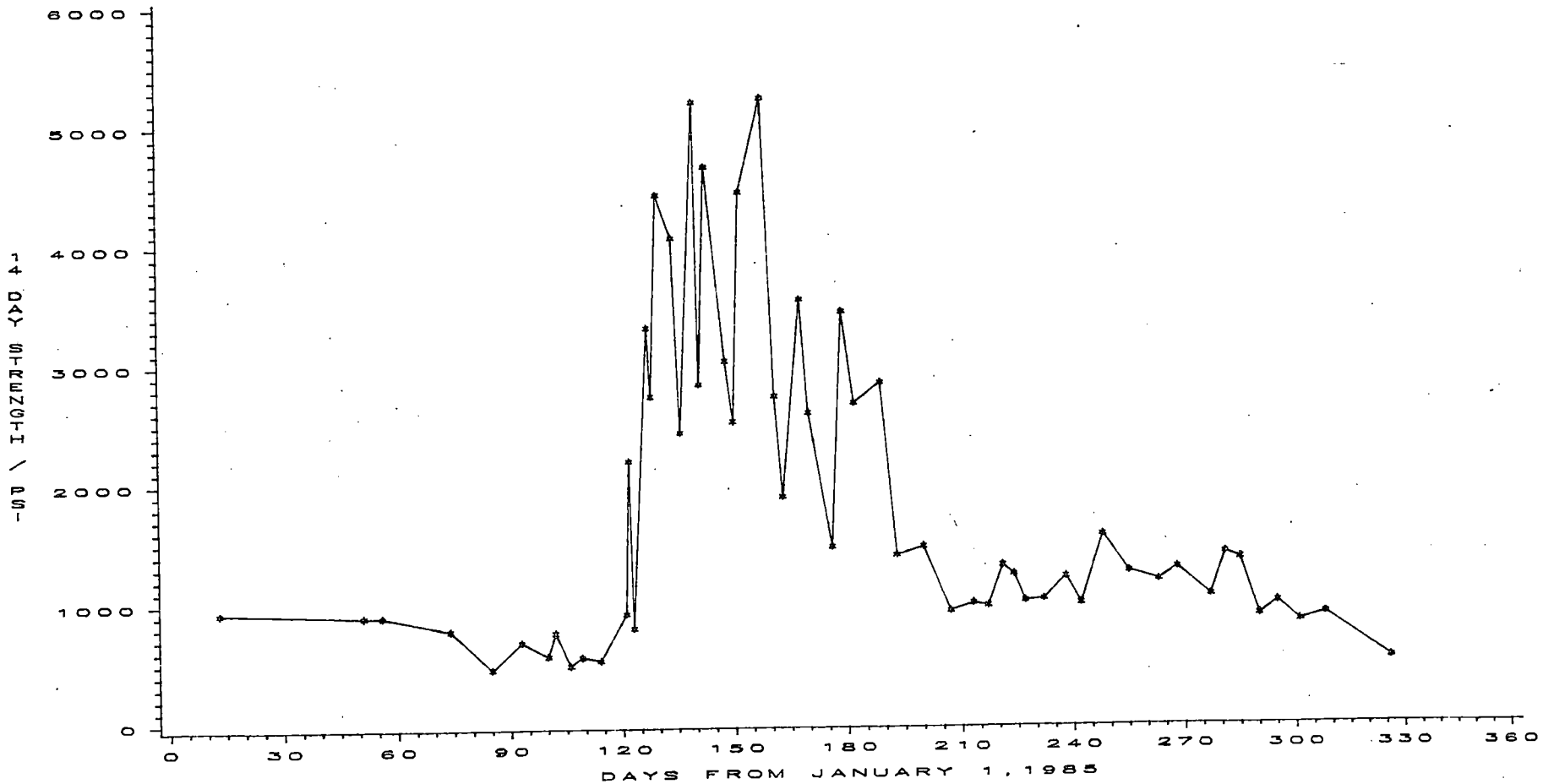
7 DAY STRENGTH VS. DAYS FROM JAN. 1, 1985

OTTUMWA FLYASH



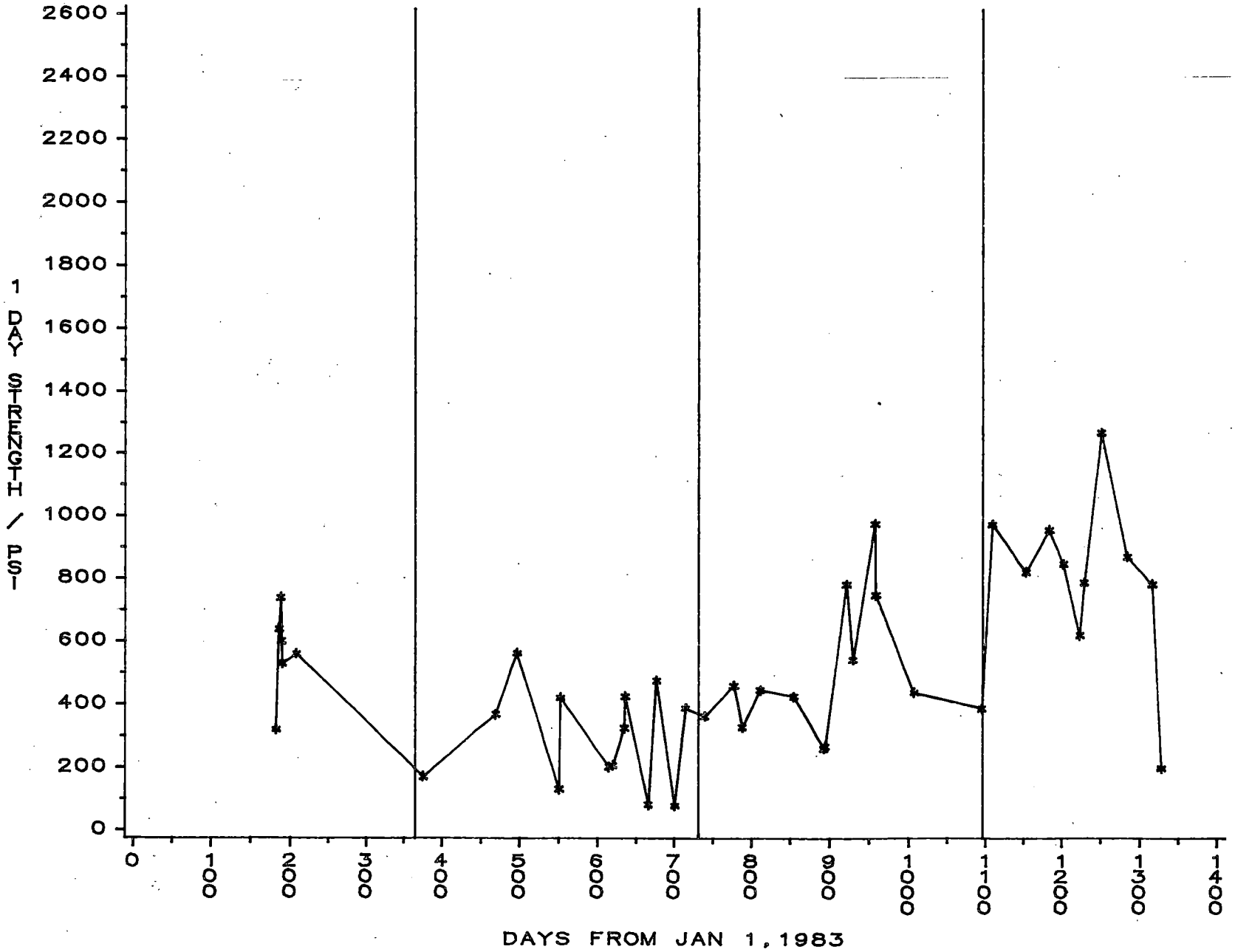
14 DAY STRENGTH VS. DAYS FROM JAN. 1, 1985

OTTUMWA FLYASH



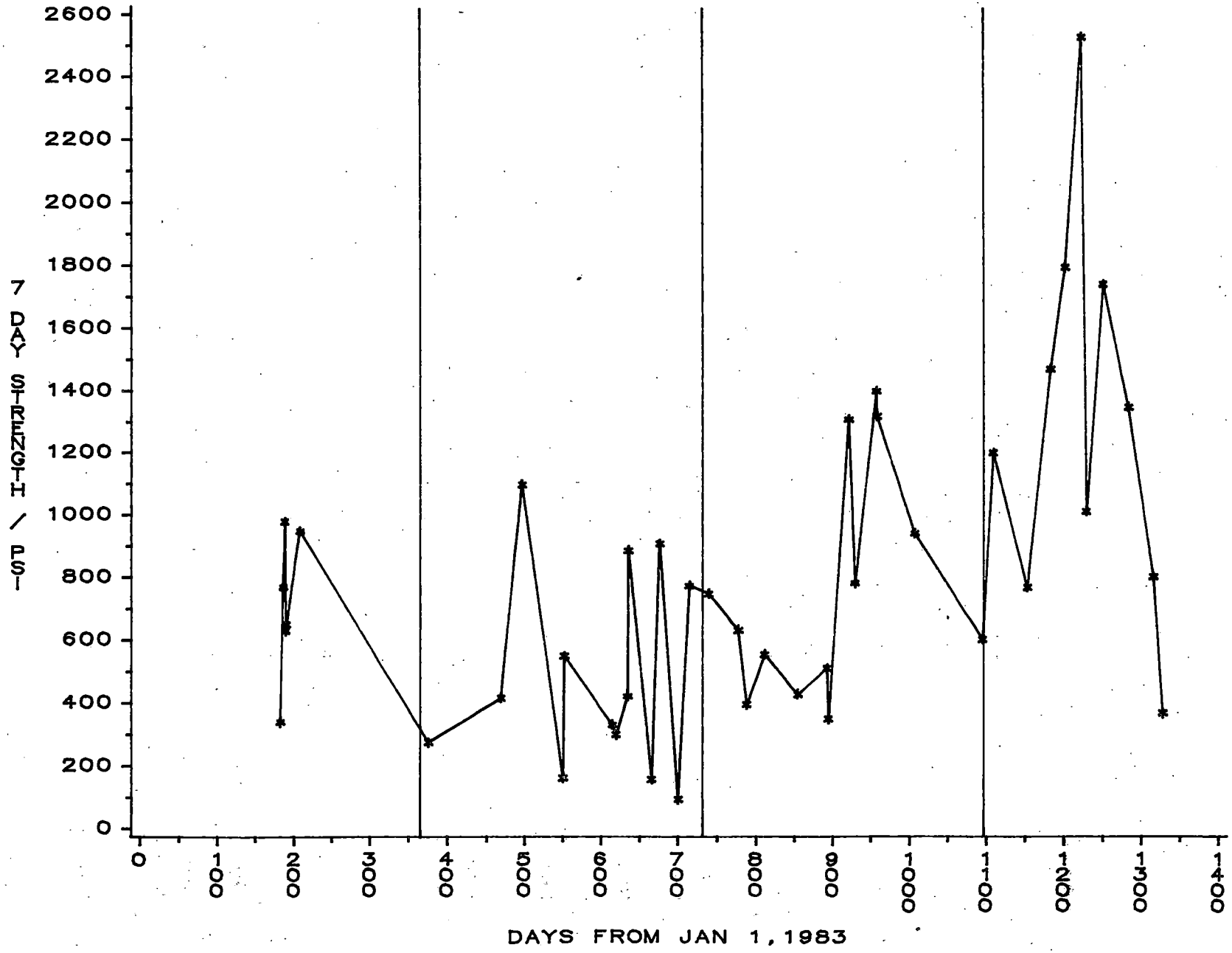
IDOT FLY ASH MORTAR CUBE STRENGTHS

COUNCIL BLUFFS FLY ASH



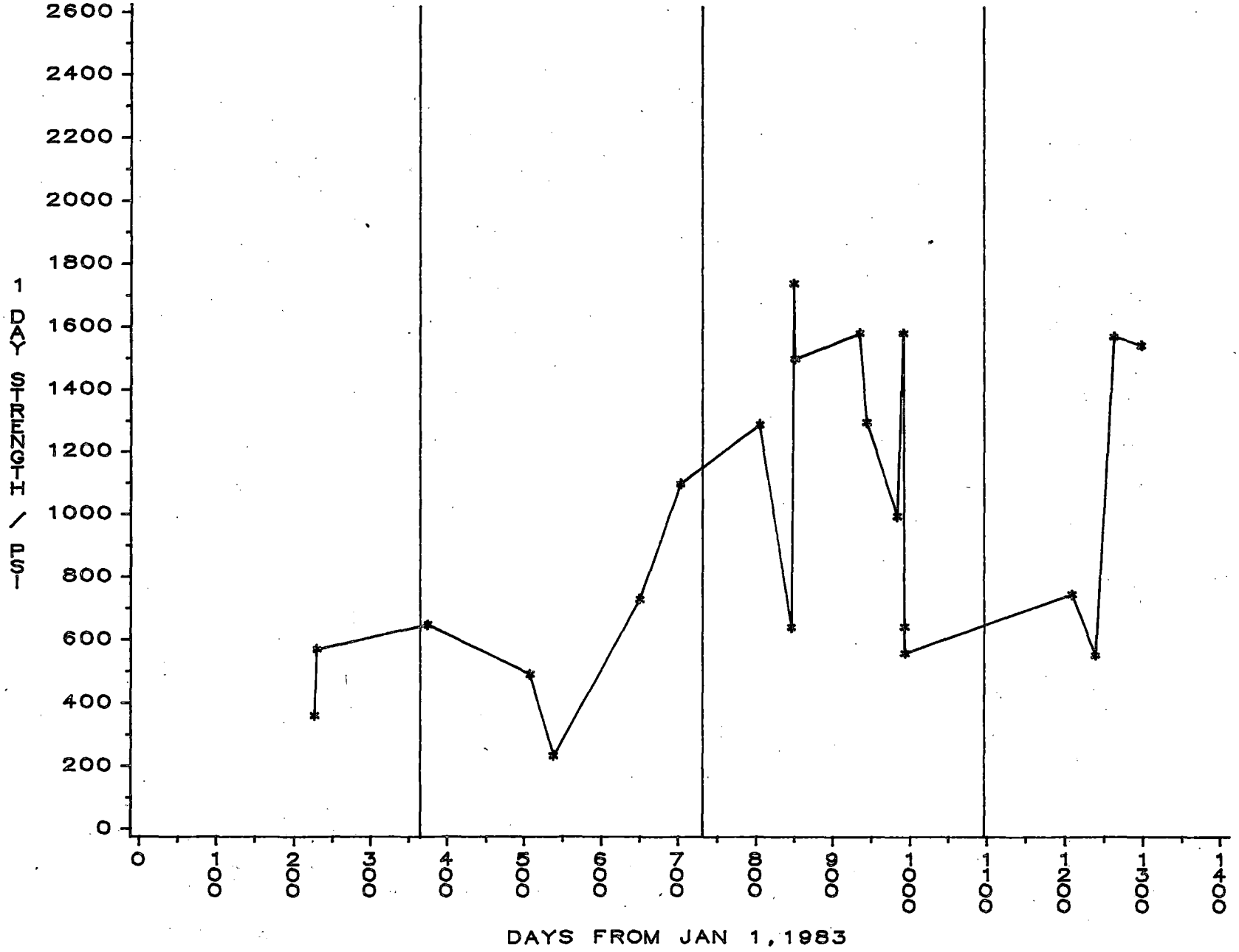
IDOT FLY ASH MORTAR CUBE STRENGTHS

COUNCIL BLUFFS FLY ASH



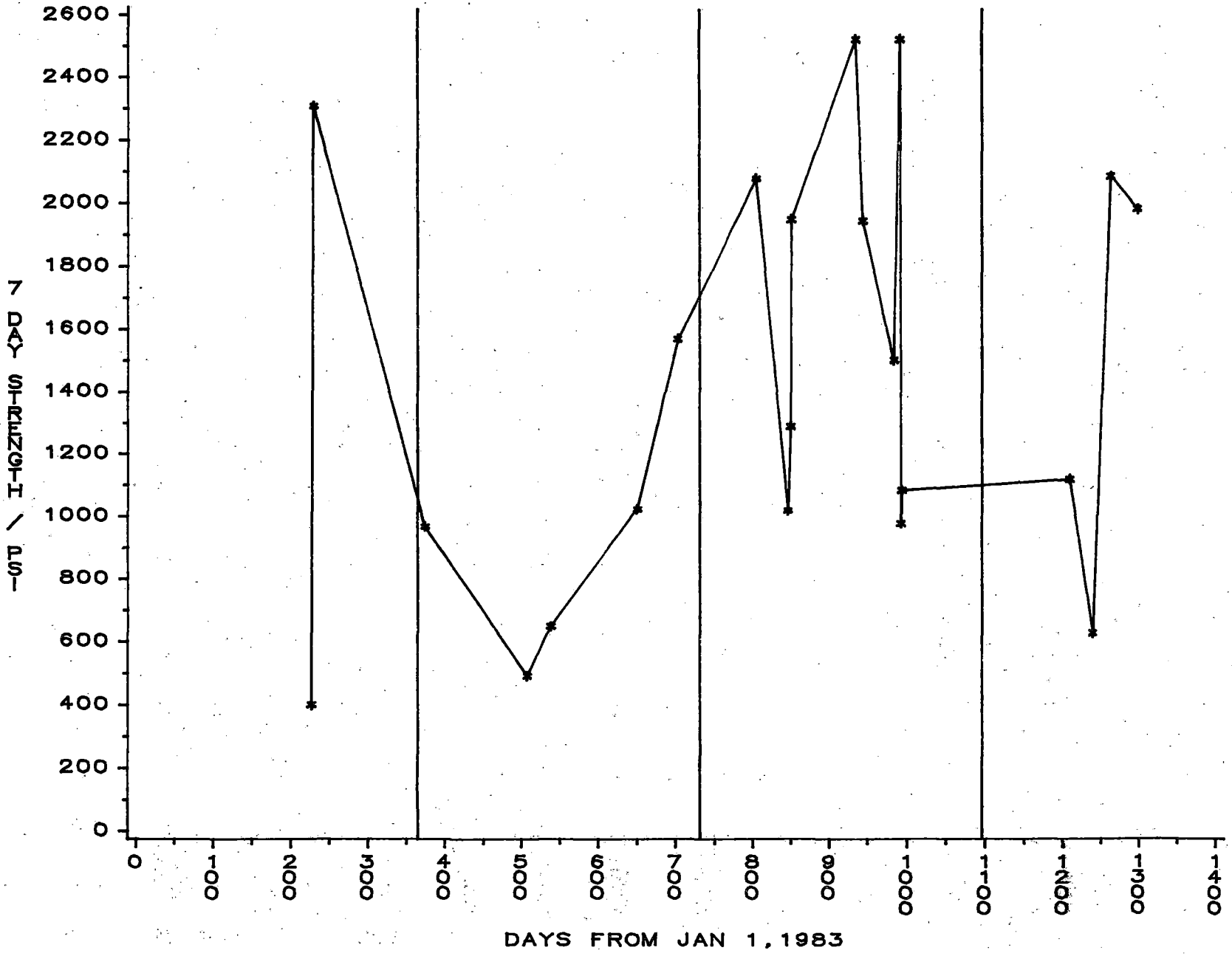
IDOT FLY ASH MORTAR CUBE STRENGTHS

LANSING FLY ASH



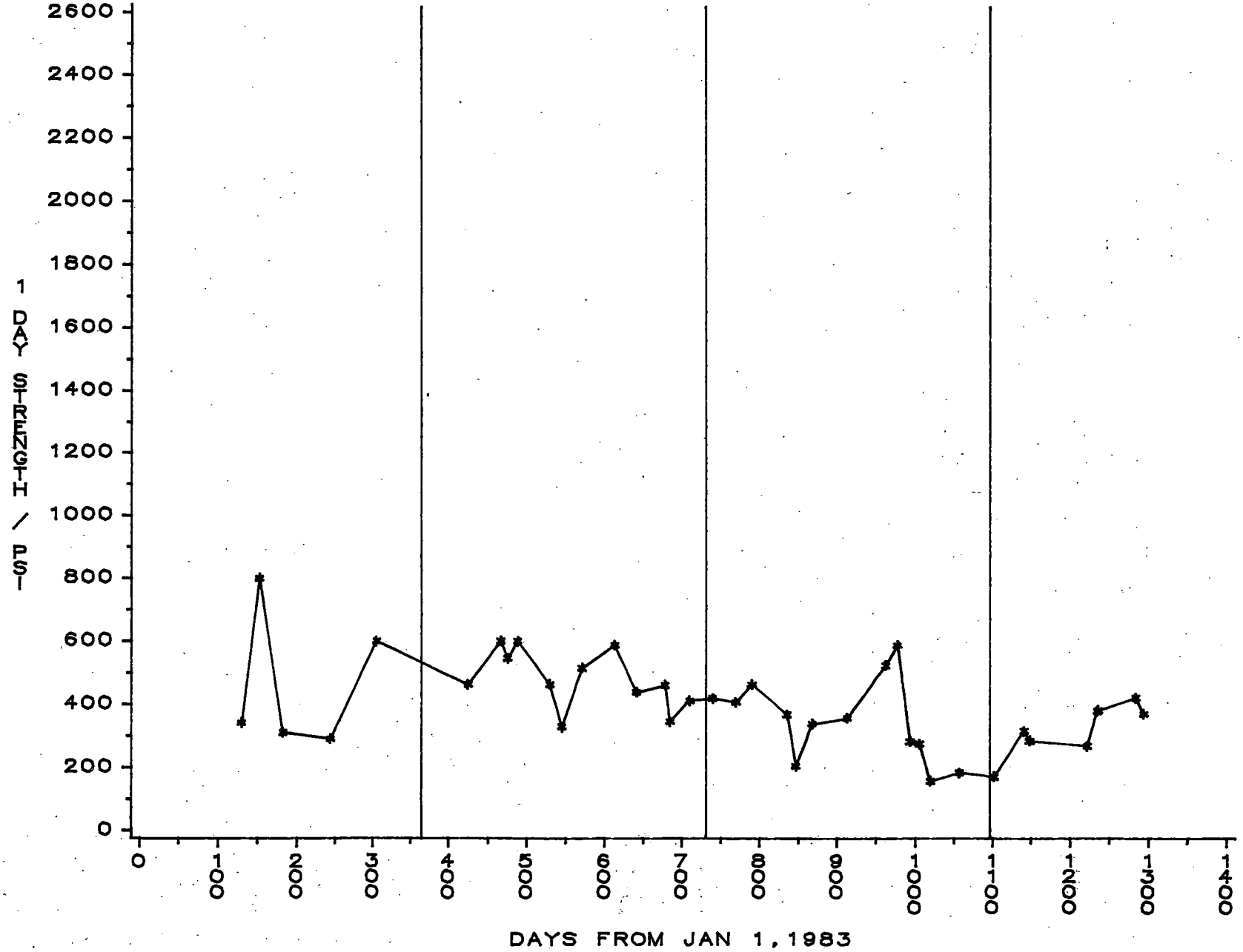
IDOT FLY ASH MORTAR CUBE STRENGTHS

LANSING FLY ASH



IDOT FLY ASH MORTAR CUBE STRENGTHS

PORT NEIL #4 FLY ASH



IDOT FLY ASH MORTAR CUBE STRENGTHS

PORT NEIL #4 FLY ASH